



**COMPARATIVE ANALYSIS OF AIRBORNE
CHEMICAL EXPOSURE TO AIR FORCE
SMALL ARMS RANGE INSTRUCTORS**

THESIS

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AFIT/GES/ENV/06M-01

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Abstract

Significant concentrations of lead can be generated at indoor and outdoor firing ranges during firing operations using conventional leaded ammunition. In an effort to eliminate the potential risk of lead exposure, the Air Force is transitioning to a lead-free alternative to the leaded bullet. This study examines airborne chemical exposure to Air Force small arms range instructors during M16 firing of lead and lead-free bullets. Historical range information collected from 63 active duty Air Force bases identified that two thirds of the Air Force military ranges within the Continental United States are currently firing lead-free ammunition. Over 420 air sampling results were compiled and statistically analyzed to determine the average representative airborne exposures during firing of leaded ammunition at indoor and outdoor firing ranges. Highest average 8-hr TWA exposures for lead were 17% of the Occupational Exposure Limit (OEL). Task exposures, representing worst case conditions, were found to be 1.2 time the OEL. Two indoor and four outdoor firing ranges currently firing frangible lead-free ammunition were evaluated through a collaborative effort with the Air Force Institute for Operational Health (AFIOH) to assess instructor exposure and current range conditions. Transition to lead-free ammunition showed a 70% reduction in lead at indoor ranges and a 41% reduction in lead at outdoor ranges. Airborne exposures generated from metals and combustion by-products associated with nylon and plastics during M16 firing of frangible lead-free ammunition were found to be well below their respective OELs. This research suggests that the exposure levels associated with lead-free ammunition does not pose a significant threat to Air Force instructors at indoor and outdoor ranges.

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Eric J. Cameron

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COMPARATIVE ANALYSIS OF AIRBORNE CHEMICAL EXPOSURE TO AIR FORCE SMALL ARMS RANGE INSTRUCTORS

I. Introduction

1.1 Background

With the terrorist attacks on the United States in September of 2001, security both in the Continental United States (CONUS) and abroad has become a top priority for this country. As author of *Profile of Munitions* R.J. Hammond states:

“Ammunition and water are the only two items that you cannot do without when locked in combat; other necessities can be provided later, if you survive.”
(Whitfield II, 1993)

Small arms originated toward the end of the 14th century as nothing more than a hand held cannon fired by placing a lighted match to its touchhole. Through time, the source of ignition mechanism in guns as well as the shape of the bullet has changed; however, the material in which it was molded has remained the same (Columbia University Press, 2003). Due to its physical properties and availability, lead has always been the main component of small arms ammunition. Its weight alone allows it to project further than any other non-leaded bullet with extreme accuracy (Vargas, 2004). Unfortunately, this ideal metal also carries with it some environmental as well as occupational health implications.

Lead triggers more Superfund cleanups across the country than any other chemical or waste product in the environment (Houlihan, 2005). Lead contamination in soil has been reported to reduce crop density, effect photosynthesis and root growth (Cao,

2003). Depending on the soil make up, small lead particles can be transported relatively quickly which can lead to further lead contamination of soils. On April 17, 2001, the Bush Administration took its first legal action, originally created by the Clinton Administration, against lead polluters. The rule required “all businesses releasing 100 pounds of lead a year (or greater) to report this pollution to the government” (Houlihan, 2005). With military draw downs and base closures, this requirement posed a significant problem for the military outdoor ranges. Soils with lead levels above Toxic Characteristic Leaching Program (TCLP) criteria are considered hazardous waste under the Resource Conservation and Recovery Act (RCRA) of 1976 and must be remediated before any closure or transfer can occur (Colorado Department of Human Health, 2005). With clean-ups of outdoor ranges being extremely tedious as well as costly, the military and other organizations are moving to indoor ranges and bullet traps to eliminate this environmental problem. Unfortunately, by containing this hazard within a hardened facility, the problem has now been transferred to the occupational arena and has become a huge health concern.

There are three possible routes in which lead can directly impact the health of personnel, more specifically small arms instructors and shooters. These routes include inhalation, ingestion and skin contact from the metal. When weapons are fired, inhalation and absorption become the predominant routes of exposure. Significant inhalation sources of particulate lead in an indoor range can be produced via the powder that starts the ignition, the lead burn of the ammunition, gun barrel friction, as well as the impact of the bullet against a steel bullet trap (Vargas, 2004). In the form of dust, fumes

or liquid aerosol, lead can be easily inhaled and absorbed through the lungs and upper respiratory tract.

Lead is a heavy metal that has a 30 year half-life in humans and is typically stored in the bones. Overexposure to lead can lead to adverse health effects in men to include decreased libido, impotence, sterility, and the potential for miscarriages and still births in women (USDHHS, 2004). Children born to parents exposed to lead have an increased chance of mental retardation as well as behavioral problems or even death within the first year of life. In addition to complications directly related with the reproductive organs, lead can also have adverse health effects on the central nervous system, the gastrointestinal tract as well as the kidneys and blood. The severity of this hazard to both the environment as well as people has driven development of alternative ammunition.

“Green”, or lead-free, bullets were primarily developed to reduce lead hazards on firing ranges. This environmentally-friendly ammunition being examined by the Air Force looks virtually identical to conventional ball ammunition, but the projectiles are made from metal powders bonded with nylon or plastics (Clark, 2000). This ammunition is available in 5.56 mm for M16 rifles as well as 9 mm for M9 pistols. In addition to being better for the environment because of the lack of lead, these bullets are also considered frangible and thus will not ricochet upon impact on hard surfaces, reducing additional airborne exposure to personnel down range as well as the potential for physical injury.

In theory, lead-free ammunition appears to be a better alternative to conventional lead bullets; however, there have been some studies that show that one potential hazard has been substituted for another. For example, tungsten green bullets used by the Army

have led to both environmental and health problems which turned out to be worse than conventional lead ammunition used previously (Vargas, 2004). Environmental and health impact studies showed a pH drop in soil, directly impacting surrounding vegetation, as well as 100% cancer rate in test rats when exposed to the tungsten fumes/particulate produced during firing range operations. With lead-free bullets being approved for Air Force use, it is only a matter of time before their use is implemented across the board. To ensure one toxic metal is not simply being replaced with another, it is essential that a critical look at these new green bullets developed to potentially eliminate environmental and health concerns is taken.

1.2 Problem Statement

Termination or transfer of firing ranges due to base closures and other circumstances has led to significant environmental concerns for the Department of Defense. Bullet traps have been implemented across the United States as a solution to reduce environmental impact to the soil at small arms firing ranges. In doing so however, the problem has now been shifted to a potential occupational health concern. This concern is amplified when ranges are enclosed and ventilation systems are found to be inadequate. Recognizing this concern, the military is taking the next step; directing the use of green bullets to eliminate the potential for lead exposure to personnel working near and firing weapons within a shooting range. In doing so, the question becomes, have we simply replaced one type of ammunition responsible for producing one toxic hazard with another that could lead to even worse adverse health effects?

1.3 Research Objectives

The purpose of this research was to conduct a comprehensive, comparative analysis of chemical exposure to instructors at Air Force small arms ranges within the United States.

Two main focus area questions and corollary questions were developed through the literature review.

(1) How many bases have transitioned to lead-free ammunition? What is the maximum and average lead exposure during small arms qualification training using both lead and lead-free bullets? How much is lead exposure reduced through the use of lead-free bullets?

(2) What other potential airborne chemical exposures have been introduced to Air Force instructors and shooters during small arms weapon qualification training as a result of the transition to green bullets?

1.4 Research Focus

There have been several studies on the health effects of the new lead-free ammunition at single ranges throughout the United States; however, the Air Force has never compiled and analyzed airborne exposures to instructors and shooters spanning all indoor and outdoor Air Force ranges within the United States. The focus of this research will concentrate around airborne chemical exposure to Air Force small arms instructors and shooters. Although environmental impact and hazardous noise exposure to military personnel are also present during shooting activities, these areas of concern will not be evaluated or analyzed within this scope of work.

1.5 Methodology

The purpose of this research was to analyze airborne chemical exposures to Air Force small arms instructors and shooters at indoor and outdoor firing ranges across the United States using both leaded and green bullets. The first step of this research effort involved identifying all potential airborne chemical hazards to both instructors and shooters during M9 and M16 Air Force Qualification Courses (AFQC). Potential constituents of concern were then identified using the Material Safety Data Sheets (MSDS)s for green ammunition fired during AFQC. Once identified, constituents were then cross referenced to determine health effects, routes of exposure, target organs and corresponding exposure limits using references put forth by the National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH), as well as the Occupational Safety and Health Administration (OSHA).

The next step was to acquire small arms range air sampling data from Air Force bases within the United States. Using information acquired during the literature review, a formal request for air sampling was compiled and coordinated through the Air Force Research Laboratory Protection of Human Subjects Branch and Major Command (MAJCOM) for support. Major commands asked to participate include Air Combat Command (ACC), Air Education and Training Command (AETC), Air Force Material Command (AFMC), Air Force Space Command (AFSPC), Air Force Special Operations Command (AFSOC), and Air Mobility Command (AMC). The Air Force Command Core System (CCS) was also utilized to capture any non responses from the field as well as serve as quality control of the data being collected. In addition to air sampling results

being requested from base level Bioenvironmental Engineering Flights across the Air Force, two bases were chosen for additional air sampling to ensure all potential airborne hazards to instructors and shooters have an opportunity to be captured. Sampling data from three bases, collected by the Air Force Institute for Operational Health (AFIOH) during green bullet use was also included in the analysis. All air sampling conducted was completed using NIOSH sampling and analytical methods.

The comparative analysis results helped identify the different types of ammunition and ammunition traps being used as well as quantify maximum and average inhalation exposure to small arms instructors and shooters across the Air Force. Air sampling techniques captured during the data call and in the literature review will serve as a starting point to develop a standardized methodology to collect future air sampling results at both indoor and outdoor ranges.

1.6 Scope and Limitations

This research was limited by the quality of data provided by base level Bioenvironmental Engineering Flights across the Air Force. Available information collected varied significantly due to the numerous differences from one firing range to the next. Variables included types of traps and ammunition, efficiency of the ventilation system, type and size of range, as well as the number of personnel firing during sampling. Due to the high turnover in personnel and minimal documentation of air sampling conditions, specific locations and range conditions for exposure levels were difficult to explain. Also, data collected from the CCS database may also contain errors and limited information regarding sampling technique and information.

1.7 Implications

In accordance with Air Force Standard Instruction (AFI) 36-2226, Air Force personnel must know how to handle firearms safely and effectively in the event of war, civil disturbance, or military conflict. In order to meet this requirement, Air Force instructors as well as shooters are required to perform duties in an area of potential health concern due to lead and other potential toxic hazards. Since all Air Force military personnel are required to qualify on their designated fire arms before being sent into combat, the Air Force stands to benefit from a comparative analysis of potential airborne exposures found at both indoor and outdoor firing ranges with green and leaded bullets. Without proper identification and quantification of potential airborne hazards to instructors and shooters within indoor and outdoor ranges, military personnel may be unnecessarily exposed to toxic hazards. Overexposure to instructors during small arms qualification training could lead to adverse health problems which could ultimately compromise mission readiness. Due to the high operations tempo of today, this is not a government resource that can be neglected. Their expertise and daily effort ensure our military force is prepared for combat.

1.8 Preview

Military firing ranges have become essential to facilitate required small arms training to prepare the men and women of our armed forces for war. The dilemma the DoD has been faced with is the potential environmental impacts introduced during small arms training at government installations. The subsequent chapters will discuss the history of the problem, the methodology used to collect and analyze the sampling data as well as present the results and recommendations gleaned from the analysis.

II. Literature Review

This chapter provides a comprehensive review of the current literature on chemical airborne exposures to instructors and shooters at small arms shooting ranges. An introduction to the basic ammunition components is provided to illustrate the make-up of the M16, 5.56 mm round being analyzed within this study. In addition, this review includes an in-depth look at the main constituent of a conventional round, lead; specifically health effects, associated blood lead levels, and current standards provided by federal agencies. This chapter further defines the sources of lead exposure and speaks to the different alternatives being implemented to reduce those exposures, mainly the use of lead-free ammunition. Findings from two analytical studies regarding the reduction/elimination of lead exposure through the use of lead-free bullets will then be qualitatively and quantitatively discussed; showing other potential toxic exposures associated with this new ammunition. Finally, a comprehensive look at the constituents that make up the specific lead-free ammunition being utilized by the United States Air Force will be provided as background information for the methodology presented in Chapter III.

2.1 Mechanism of Operation

All conventional ammunition rounds are made up of two major components, the projectile and the cartridge as shown in Figure 2.1. The projectile is made up of a dense material, typically lead, and is often defined by a tip on its leading edge for target penetration. The cartridge's primary function is to house the propellant and primer for activation upon impact of the firing pin. The M16 rifle fires a 5.56 caliber fixed round

and is considered a small arms weapon. Small arms ammunition is defined as any round less than or equal to 50 caliber. Webster defines ammunition as being fixed when the cartridge casing is permanently attached around the base of the projectile to form one solid unit (Nielson, 1944).

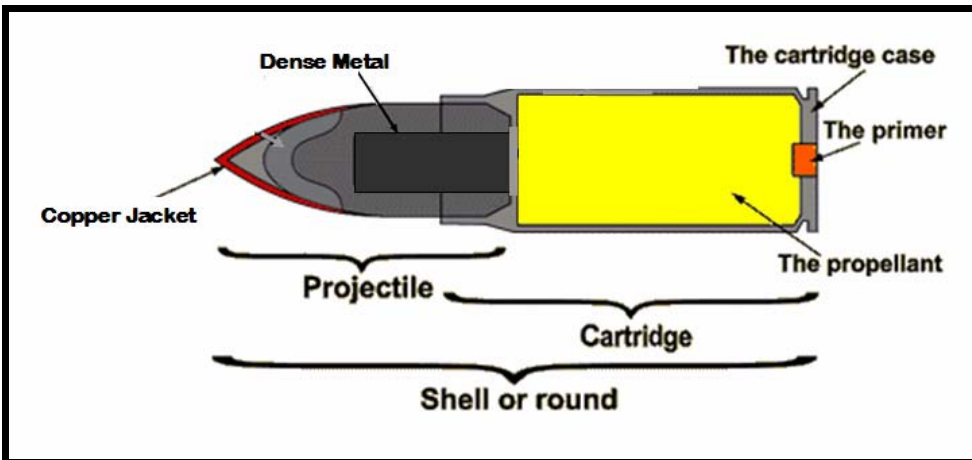


Figure 2.1 Bullet Components (Potapov, 2005) Conventional ammunition rounds are comprised of two parts, the projectile and the cartridge.

In order to identify and quantify airborne chemical exposures to Air Force instructors and shooters within indoor and outdoor shooting ranges, it is first critical to have a clear understanding of the physical process taking place during normal firing operations. There are several steps in the process including loading the bullet into the weapon, chambering the round, pulling the trigger and releasing the firing pin. Once struck by the firing pin, the primer explodes causing the propellant in the cartridge to ignite. The burning propellant in conventional ammunition can generate pressures typically ranging from 18,000 to 20,000 pounds per square inch (psi) and temperatures of roughly 2000 degrees Fahrenheit (Department of the Navy, Dec 1999). As the gas in the

bullet expands, the bullet is propelled down the length of the barrel in the direction of the target. By scoring the inside of the barrel with spiral grooves called rifling, the bullet is forced to spin as it travels down the barrel and thus resists tumbling in flight. An illustration identifying key components of the M16 rifle is provided in Figure 2.2. In addition to understanding the flight path of the ammunition, it is also imperative to briefly discuss the basic configuration of both inside and outside ranges to better understand the working environment of Air Force instructors.

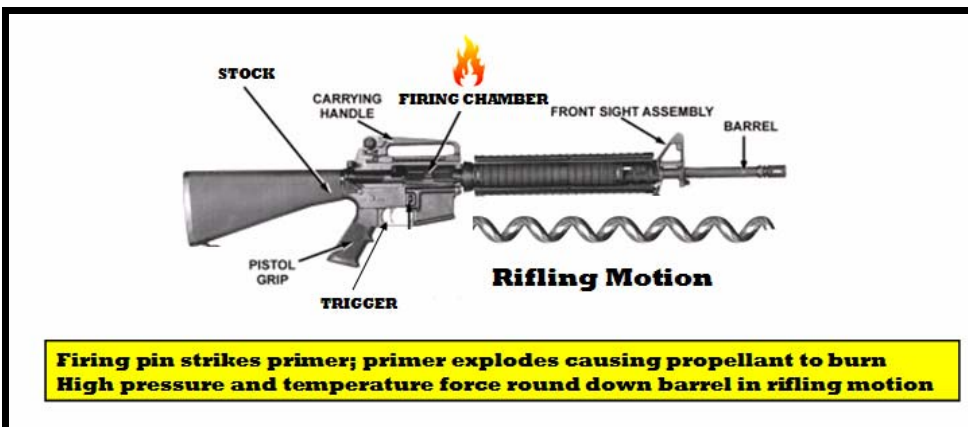


Figure 2.2 M16 Key Components and Mechanism of Operation (HQ Department of the Army, 1993).

2.2 General Range Configuration

Military indoor and outdoor small arms ranges are designed to facilitate firing operations of the M9 pistol and M16 rifle. At a minimum, the general configuration of an open outside range consists of a firing line and a target down range. While the length of the ranges may vary from 50 to 100 feet in length, typical lengths for new ranges will be roughly 84 feet (Department of the Navy, 1999). If space is not abundant, earth mounds or backstops can be added down range from the shooter to help stop expended rounds once they have been fired from the weapon and penetrated their target. Conventional

earth berms and backstops at outside ranges usually range between 25 and 30 feet in height (Mullins, 2001). Space between individuals firing should be designated by firing lanes extending four to five feet in width (Department of the Navy, 1999). Combat Arms training ranges designed for Air Force qualification training will have barriers installed on the firing line in the middle of these firing lanes so shooters may conduct over the barrier firing. Over head covers and baffles may also be installed at a shooting range to protect shooters, instructors and innocent bystanders from ricocheting bullets and inclement weather (Mullins, 2001). In addition to conditions found at outdoor ranges, indoor ranges may also have rubber mats for shooters to fire from the prone and kneeling position, additional lighting, automated target retrieval systems, baffles to protect overhead lighting as well as mechanical ventilation systems to draw away unwanted contaminants created during firing operations (Department of the Navy, 1999).

Since the speed and distance of a bullet projected from a weapon is dependent on the specific characteristics of the ammunition being fired, lead has traditionally been used in conventional rounds. Given that conventional bullet projectiles are made primarily of lead and the primers contain lead as well, sources of generation as well as the health effects associated with this highly toxic heavy metal must also be discussed.

2.3 Lead

Individuals using conventional ammunition during small arms firing operations are potentially at risk of being exposed to lead through four specific sources of generation. Traditionally, conventional bullets were manufactured with a primer containing lead styphnate (Commonwealth of Massachusetts, 2005). This component was chosen to better initiate the explosion in the propellant over other compounds such as

mercury fulminate and lead azide. Lead styphnate was better able to resist shock and friction leading to a more consistent ignition. The drawback to using lead styphnate is the potential for lead oxide fumes being produced during combustion (Fischbein, 1979; Commonwealth of Massachusetts, 2005). Once the primer is struck, the next potential source of lead exposure results from the extreme environment created from the burning of the propellant in the cartridge. As temperatures exceed 1100 °F, the lead projectile sitting in front of the propellant will begin to vaporize and the resulting fume may be inhaled by the shooter or instructor within the vicinity of the weapon. In addition, lead dust may be generated as the bullet rapidly rifles down the length of the barrel due to friction created between the projectile and the barrel or by misalignment problems with the “barrel, cylinder, clip, or magazine (Department of the Navy, Dec 1999). The final source of lead exposure, in the form of dust and lead oxide fumes, comes from the termination of the bullet as it strikes a hard target, bullet trap, or back stop (Fischbein, 1979).

2.3.1 Health Effects of Lead

Lead can have numerous adverse effects on the human body. At firing ranges, it enters into the body primarily through ingestion or inhalation. Once within the body, lead can be absorbed into the bloodstream and accumulated longitudinally over the life of the individual being exposed. “Approximately six percent of all lead ingested or inhaled is immediately deposited into the blood or soft body tissues, such as the kidneys, brain or other vital organs” (OIG DoD, Aug 98). The rest is deposited deep into the bone marrow where it is stored for roughly 20 years due to its relatively long biological half-life (Gulson 2002). After the lead is metabolized, it will eventually be excreted out of the

body through the urine, bile, sweat, hair and nails (OIG DoD, Aug 98). While in the body, lead has no beneficial function. The degree to which the body is affected by lead is directly related to the duration and amount of exposure.

Acute overexposure to lead, at high enough doses, can lead to death in as short a time as a few days (OFRNAR, 2004). At a high enough concentration, an individual can develop a condition referred to as encephalopathy in which lead has directly damaged the brain. Although rare, an individual with this condition may experience seizures, coma, and even death from cardio-respiratory arrest. Although health effects and developing diseases caused from short term high exposure are a big concern, individuals at firing ranges are more likely to be exposed to lower concentrations of lead over a prolonged period of time.

Chronic overexposure to lead can severely damage many of the soft tissue organs as well as negatively impact an individual's blood and reproductive systems. Individuals experiencing chronic lead overexposure will typically show symptoms of "loss of appetite, metallic taste in the mouth, anxiety, constipation, nausea, pallor, excessive tiredness, weakness, insomnia, headache, nervous irritability, muscle or joint pain or soreness, fine tremors, numbness, dizziness, hyperactivity, and colic" (OFRNAR, 2004). Like acute overexposure, chronic overexposure can also damage the Central Nervous System (CNS) and lead to encephalopathy. In conjunction with its effect on the brain, overexposure to lead may begin to weaken the bones and ultimately result in paralysis (OFRNAR, 2004). Precursor symptoms to the most severe form of this condition often include but are not limited to vomiting, drowsiness, memory loss, restlessness, and convulsions (OFRNAR, 2004).

The urinary system within the body is also affected by overexposure to lead. Unlike the CNS, symptoms of damage occurring to the kidney do not exist. Even with routine laboratory tests, it is rare to detect any damage to the kidneys until roughly two-thirds of their function has been lost (OFRNAR, 2004). Once this occurs, it is very likely that other organs will begin to fail. In the reproductive system, lead can cause problems to both men and women. In men, it can decrease sex drive and lead to impotence, sterility, and the alteration of sperm (OFRNAR, 2004). These effects increase the risk of birth defects in future children dramatically. Studies have shown that direct and indirect overexposure to women may lead to miscarriages or stillbirths (OFRNAR, 2004). In addition to complications prior to birth, children born to parents working with or around lead also have an increased risk of experiencing “birth defects, retardation, behavioral disorders” and in some cases death within the first year of life (OFRNAR, 2004). Individuals who are overexposed to lead will also experience alterations in the blood which can lead to anemia. Due to the decreased oxygen carrying capacity, individuals will again become tired and weak with little to no physical effort.

2.3.2 Blood Lead Levels

While lead concentrations found in urine, teeth and hair can be used as biological indicators of exposure, blood levels are currently the best way to monitor biological exposure to lead due to the strong correlation between symptoms and exposure levels (USDHHS, 1997). Blood lead levels illustrate the current amount of lead present within an individual’s bloodstream at any given time. This snapshot analysis has proven to be reliable in indicating the amount of absorption into the bloodstream, but does not, however, account for previous exposures. This test also does not represent the amount of

blood stored in the soft tissues mentioned previously, only that which is within the bloodstream itself. Other blood tests used to screen for lead poisoning include erythrocyte protoporphyrin (EP) and zinc protoporphyrin (ZPP) tests. Unlike the blood lead level test, these tests are both designed to assess chronic effects attributed from lead and are typically representative of exposure over a 3 to 4 month period (Novotny, 1987; AACC, 2004). EP and ZPP levels are representative of biological events occurring in the bone marrow (Fischbein, 1979). Skeletal bone tests are also being used to determine cumulative lead exposure for individuals chronically exposed to lead (USDHHS, 1997).

Numerous studies on blood lead level exposure allow us to predict if individuals will be at higher risk for lead related health problems. Currently, 29 CFR 1910.1025 Occupational Safety and Health Standards, suggests this threshold limit to be roughly 40 micrograms per deciliter ($\mu\text{g/dl}$). Due to the infinite variable responses possible between individuals, this dose level is only an estimated level of concern. Table 2.1 summarizes some of the blood lead level ranges correlated to specific health effects and symptoms mentioned previously. A comprehensive table listing all blood lead level correlations and the specific references can be found in Appendix A (USDHHS, 1999).

With the Air Force down-sizing to a leaner force, small arms firing instructors must be able to perform their duty routinely in order to meet mission operation requirements. A long absence in duty could hinder readiness training of the men and women preparing for combat. In order to ensure the protection of the instructors as well as shooters at shooting ranges, a preventative approach has been taken to evaluate lead exposures. Historically, and currently, range evaluations are being evaluated through the

Table 2.1. Blood Lead Level Ranges and Associated Health Effects
(USDHHS, 1999; Commonwealth of Massachusetts, 2005)

Health Effect	Blood Lead Level (µg/dL)
Severe Brain Damage (Encephalopathy)	50 – 300
Headaches, memory and concentration problems, sleep disturbances, mood changes	40 – 80
Anemia	60
Stomach pain, constipation, diarrhea, loss of appetite	50 – 70
Nerve disorders; decreased red blood cells	40 – 80
Male reproductive problems; kidney damage	40 – 50
Slower reflexes	30
Harmful effects on the fetus; impaired mental development	10 – 15

local Bioenvironmental Engineering Flight at each base operating small arms ranges.

Evaluation for lead exposure to military personnel is typically performed through airborne sampling. Airborne lead samples are analyzed in accordance with specific analytical methods, to be discussed in Chapter III, and then compared to a standard for compliance. Controls, such as improved ventilation or more advantageous instructor positioning are then implemented to reduce any high exposures.

2.3.3 Standards and Regulations

Because of the large concern with overexposure to lead and its associated health effects, a number of federal agencies have established specific standards or occupational exposure limits (OELs) to protect personnel working in lead environments. An OEL is simply a reference value established for a specific chemical substance in the air thought

to have no adverse health effects for a specified time (Department of the Air Force, 1997). Table 2.2 summarizes these standards for lead in specific media.

Table 2.2 Summary of Standards and Regulations for Lead (USDHHS, 1999)

Agency	Media	Level	Comments
Occupational Safety and Health Administration (OSHA)	Blood	40 µg/dL *	Regulation; cause for written notification and medical exam
		50 µg/dL *	Regulation; cause for medical removal from exposure
	Air (workplace)	50 µg/m ^{3†} 30 µg/m ³	Regulation; permissible exposure limit (8-hr average) (general industry) Regulation; action level
National Institute for Occupational Safety and Health (NIOSH)	Air (workplace)	50 µg/m ³	Advisory; recommended exposure limit for 10 hour work day (non-enforceable)
		100 mg/m ³	Advisory; immediately dangerous to life and health
American Conference of Governmental Industrial Hygienists (ACGIH)	Air (workplace)	50 µg/m ³	8-hr TLV/TWA guideline for other forms of lead
	Blood	30 µg/dL *	Advisory; biological exposure index
US Environmental Protection Agency (EPA)	Air (ambient)	1.5 µg/m ³	Regulation; National Ambient Air Quality Standard; 3-month average
*µg/dL: micrograms per deciliter. †µg/m ³ : micrograms per cubic meter. ‡TLV/TWA: threshold limit value/time-weighted average.			

In accordance with the Air Force Occupational Safety and Health (AFOSH) Standard 48-8, Controlling Exposures to Hazardous Materials, the Air Force will adopt the most stringent standards set forth by the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), and the American Conference of Government Industrial Hygienists (ACGIH). OSHA has set an enforceable permissible exposure limit (PEL) for airborne lead in the

workplace of $50 \mu\text{g}/\text{m}^3$ as an 8-hour Time Weighted Average (TWA) (USDHHS, 1997). Since a TWA is the amount of time a given exposure is averaged over, then a PEL 8-hour TWA is the average value of exposure of a given substance that should not be exceeded over the course of any 8-hour period (OFRNAR, 2004). NIOSH, responsible for recommending health and safety standards, has published a slightly less stringent recommended exposure limit (REL) of $50 \mu\text{g}/\text{m}^3$ as a 10-hour TWA, as well as an exposure limit of $100 \text{mg}/\text{m}^3$ under immediately dangerous to life and health (IDLH) conditions. An IDLH exposure condition is defined by NIOSH as a condition “that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment” (US Department of Human Health and Services, 1997). In addition to the government agencies previously mentioned, the ACGIH, a professional society, has also published a recommended threshold limit value-time weighted average (TLV-TWA) of $50 \mu\text{g}/\text{m}^3$. The TLV-TWA is defined as “the time-weighted average concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effects” (ACGIH, 2002).

Most airborne chemical hazards shown to cause adverse health effects typically have an action limit (usually one-half the permissible exposure level) established to indicate an airborne concentration level of concern. By establishing an action level, employers have an opportunity to take preventative action before an employee is required to stop working in the unsafe environment because of health problems. For lead, OSHA has set an action level of $30 \mu\text{g}/\text{m}^3$ as an 8-h TWA with exposures of more than 30 days

per year. In the event this level is exceeded, an employer is mandated “periodic determination of blood lead levels” (USDHHS, 1999). Furthermore, if an employee is found to be at or above the OSHA airborne action level and their last three blood lead levels were found to be over 50 µg/dL, then an employee is required to be removed from this environment by his employer in order to protect the worker’s health (OFRNAR, 2004).

While OSHA, NIOSH and ACGIH are primarily noted as the agencies established to protect worker health, the Environmental Protection Agency (EPA) has also set a lead standard in response to the National Ambient Air Quality Standards (NAAQS) requirement outlined in the Clean Air Act as amended in 1990 (U.S. EPA, 2005). The EPA standard of 1.5 µg/m³ is designed to not only protect healthy adults, but also to include children, the elderly as well as any individual with sensitive conditions. Unlike the 8-hour average exposure standards brought forth from the public health agencies mentioned previously, this environmental standard is averaged over a three month period.

2.3.4 Lead Ammunition Studies

Numerous studies have confirmed a positive correlation between the use of conventional lead ammunition, elevated lead exposures, and lead absorption in instructors and shooters at indoor and outdoor firing ranges. Based on similar methodologies, blood lead levels and airborne lead concentrations were recorded to serve as a baseline record of exposures for personnel working or firing at each range (Center for Disease Control and Prevention, 2005; George, 1993; Novotny, 1987; Fischbein, 1979). Suspending the use of fire arms in every case resulted in a significant decrease in blood lead levels and/or airborne lead concentrations. Individuals performing maintenance or range clean up were

found to experience higher lead levels relative to other employees (Novotny, 1987). In addition to employees exposed to high lead levels over a short period of time, those working with greater frequencies and longer durations were also found to have increased lead levels over workers with less time invested at the range. Specific findings and quantitative values for each study are presented in the comprehensive summaries to follow.

The Alaska Environmental Public Health Program conducted a comprehensive study to evaluate lead exposure for high school shooting teams at indoor firing ranges within central Alaska (CDC, 2005). Participants in this study included 66 students from five different shooting ranges. Blood lead level (BLL) tests were conducted to quantify levels of lead exposure. Average BLLs for team members at one firing range spanned from 21 to 31 $\mu\text{g/dL}$ with a mean BLL of 24.3 $\mu\text{g/dL}$. Non-shooting members from the same households were also tested during this study. All results for non-shooting members resulted in a mean BLL between 2.6 and 3.5 $\mu\text{g/dL}$ and would suggest that no additional sources of lead exposure were being introduced to the students at home or from extracurricular family activities. Participants' mean BLLs from the other four firing ranges ranged from 2.1 $\mu\text{g/dL}$ to 18.5 $\mu\text{g/dL}$. Upon completion of the BLL test, team members were removed from this environment for a 3-month period and then retested for comparison to their original BLL test. Suspending the use of fire arms in every case where pre- and post- BLL tests were performed resulted in a significant decrease in mean BLLs ranging from 23.6 - 41.2%.

Airborne lead exposure and elevated lead levels found in recreational shooters at Christchurch Targeting Club in New Zealand suggest that lead is a significant problem at

indoor ranges. Fifty-two out of 120 target shooting club members were studied in the early 1990's for lead exposure over the course of a one year period (George, 1993). BLLs were measured at the end of a six month long season and again prior to the start of the new season six months later. Results showed an average reduction of 56% in BLLs prior to the start of the new season indicating these firing ranges served as a significant source of lead exposure. Findings from air sampling for lead and bulk dust samples provided additional data to support the presence of lead in this environment. At one range, accumulated dust contained roughly 24-36% lead while background dust from a nearby city was only 0.1% lead.

The Colorado Health Department was notified in 1985 of two indoor firing range workers with elevated BLLs (Novotny, 1987). Employees' BLLs were "88 and 69 $\mu\text{g/dL}$ " respectively. In response, BLL and EP tests were performed for the employees with elevated BLLs, the other two employees working at the range, as well as three of their spouses to determine both the acute and chronic exposure caused from working at the range. "Levels greater than or equal to 30 $\mu\text{g/dL}$ for the BLL test were considered evidence of recent lead exposure while levels greater than or equal to 50 $\mu\text{g/dL}$ for the EP test showed evidence of lead exposure over a 3 month period". Blood lead levels for the four employees ranged from 41 to 77 $\mu\text{g/dL}$ and 24 to 244 $\mu\text{g/dL}$ for the EP test indicating fairly recent elevated lead exposures. The range manager, whose additional duties included cleaning the range, was identified to have the highest levels of lead exposure. Symptoms experienced by this individual included intermittent headaches and numbness and weakness in his left leg. After refraining from cleaning the range and avoiding exposure during firing for a four-month period, the range manager was able to

reduce the amount of lead absorbed in his body (as evidenced by a 41% reduction in blood lead level) as well as eliminate all previous symptoms with the exception of a minor calf tremor. Other employees tested also showed a significant reduction in exposure. Levels of lead exposure were significantly affected by the duration of time spent in the range. Employees working full time showed a higher exposure than those only working part-time. No association was made between smoking or eating within the range due to the small number of employees sampled. In addition to blood tests, area sampling was conducted to determine the extent of airborne lead exposure within the range. Air sampling pumps were set-up at various locations ranging from the firing line to the target. Air sampling over an eight hour period showed increasing airborne concentrations as the target area was approached. Samples taken at the target as well as midway between the firing line and the target were found to be above the OSHA permissible exposure level of $50 \mu\text{g}/\text{m}^3$.

A study of law enforcement agencies in New York took an in-depth look at the duration and frequency of employment and associated medical symptoms (Fischbein, 1979). Results showed a proportional relationship between Central Nervous System (CNS) symptoms and the number of years of employment. For example, 50% of all law enforcement officers working 10 or more years at the indoor range reported CNS symptoms while only 22.5% of officers working less than 5 years in duration reported similar symptoms. In addition, increased hours spent at the firing range, regardless of years of employment, were also noted to increase the instances of CNS symptoms. Cases of gastrointestinal (GI) symptoms showed a similar correlation with the number of years an individual was employed at a shooting range.

Blood samples were taken to measure blood lead levels for instructors employed at both indoor and outdoor ranges (Fishbein, 1979). The duration of exposure for instructors working in each type of environment was four months. Mean BLLs during indoor and outdoor training periods showed a significant difference in exposure to the instructors. Indoor and outdoor exposures were found to be 31.9 µg/dL and 41.2 µg/dL, respectively. ZPP lead levels, however, showed little to no change between the two shooting environments. Results of these tests indicated that the average exposure over the four month period remained relatively constant but the instantaneous levels captured using the BLLs showed an increase in exposure.

Although attention has been focused on lead exposure at indoor ranges, this does not rule out the potential for hazardous effects of lead at uncovered or partially covered ranges. Studies have shown that outdoor ranges with heavy firing operations can also experience significant levels of airborne lead (Goldberg, 1991). In addition, lead exposure to individuals working at outdoor ranges can fluctuate significantly due to changes in environmental conditions (Goldberg, 1991). Seasons producing calm or stagnant air movement may contribute to personal exposure while other seasons conversely may produce more turbulent winds which could likely move a given contaminant away from the breathing zone. While winds can provide a positive control through natural ventilation, they may conversely force the same contaminant back into the breathing zone of the individual thus compounding the potential for increased inhalation exposure.

2.3.5 Other Concerns

In addition to lead, other compounds generated during conventional firing operations are noteworthy. These combustion by-products include “nitrogen, hydrogen, carbon dioxide, nitrogen oxide, and complex organic compounds of nitrogen” (Fischbein, 1979) as well as carbon monoxide. Primarily an eye irritant, these by-products can also cause breathing difficulties for humans at higher concentrations. While one individual firing an M16 does not necessarily present a significant health hazard, multiple personnel firing over 100 rounds each, however, may lead to significant levels of concern over time if adequate ventilation is not in place.

2.4 Alternatives for Reducing Exposure to Airborne Lead

By implementing engineering and administrative controls, instructors in most instances are able to reduce or in some cases eliminate lead exposure all together. One easily implemented administrative procedure that is often overlooked is the simple practice of hand-washing which reduces the potential of lead ingestion. Other administrative controls commonly used to reduce lead exposures of instructors and shooters include reducing duration and frequency of work at the range as well as contracting out regularly scheduled range cleanings. Ranges with infrequent or improper cleaning procedures can lead to the resuspension of dust increasing the potential risk of lead exposure to instructors as well as future shooters (Common Wealth of Massachusetts, 2005). While administrative controls can in fact be a quick and simple way to reduce exposures, engineering controls are the preferred method of controlling a hazard. Engineering controls shown to reduce lead exposure include ventilation systems

for indoor ranges, automated target retrieval systems, special bullet traps, as well as alternative ammunition.

2.4.1 Ventilation and Automated Retrieval Systems

Unlike outdoor ranges exposed to variable wind speeds and direction, enclosed facilities have the unique ability to maintain a relatively steady environment. Use and maintenance of an adequate ventilation system can be a key component in controlling airborne exposures to shooters and instructors at indoor ranges. A study conducted to evaluate lead exposure for Alaskan shooting teams at five independent indoor ranges attributed elevated lead levels to “improper design and maintenance as well as poor ventilation systems”(Center for Disease Control and Prevention, 2005). Individuals designing a ventilation system for indoor shooting ranges should always ensure that the system will control the potential hazard of concern below its OEL. To meet this criterion for lead, NIOSH recommends a flow rate greater than or equal to 50 feet per minute at the firing line (U.S. Department of Health, Education and Welfare, 1975). In addition, the ventilation system should be balanced in order to maintain a steady airflow across the shooters back. An unbalanced system will form eddies which can actually redirect the airflow back at the shooter or instructor behind the firing line and increase the potential for airborne lead exposure (Fischbein, 1979). Use of a target retrieval system in conjunction with adequate ventilation can further reduce potential exposures by preventing the unnecessary movement of instructors and shooters past the firing line where lead hazards may be concentrated down range (Department of the Navy, December 1999).

2.4.2 Bullet Traps

In 1999, the Action Target Total Contaminant Trap (AT TCT) was identified as the most common bullet trap utilized within AETC (Kirsch, 1998). See Figure 2.3 for an illustration of the AT TCT. Although there are many different variations of this technology, the general purpose of a bullet trap is to capture the spent round once it has been discharged from a weapon. The AT TCT accomplishes this by directing the bullet through a linear funnel and into a deceleration chamber. This unit is designed to capture major fragments from the bullet as well as the lead dust generated upon impact. If maintained properly, this equipment, in conjunction with a good ventilation system, can serve as a useful tool to control lead exposure up-range where instructors and shooters perform their duties. Individuals responsible for the routine cleaning and maintenance of these traps, however, will likely increase their risk of potential lead exposure generated from dust. Routine cleaning and High Efficiency Particulate Air (HEPA) filter changes for this system will vary depending on the quantity, frequency and climate of firing operations. In more humid climates, dust has a tendency to build up and clog filters which can have a significant effect on its efficiency.



Figure 2.3 Action Target Total Containment Trap (Action Target, 2005). The AT TCT was identified as the most common containment trap used within AETC.

2.4.3 Jacketed Bullets

Originally designed to improve the flight and speed of the round as it travels down the barrel of the weapon, the introduction of the jacketed bullet has also shown a significant contribution to reducing lead exposure at the source. Typically made with a copper alloy, these jacketed rounds serve as a barrier to totally encapsulate the lead core of the conventional bullet. One study has shown that firing totally copper-jacketed bullets can reduce airborne lead concentrations by a factor of 21 over that of conventional lead bullets (Tripathi, 1990). Other studies showed a positive reduction in airborne lead concentrations ranging from 60% to 89% (Goldberg, 1991; Tripathi, 1991). Associated blood lead levels of shooters participating in Goldberg's study dropped significantly from over 50 µg/dL to less than 40 µg/dL within a three month period after shooting began using the copper-jacketed bullets. Although lead reduction can be achieved using these alternative bullets, total elimination of lead exposure is highly unlikely. As mentioned previously, hot gases produced as a result of the burning propellant can cause lead projectiles to vaporize. Due to these extreme conditions, even copper-jacketed bullets "may be vaporized if the base of the bullet is not jacketed" (Navy Environmental Health Center, Dec 1999).

2.5 Lead-Free Ammunition

The only way to completely eliminate lead exposure to instructors and shooters during firing operations is to transition to a lead-free round. Aware of the environmental concerns generated by conventional lead bullets, manufacturers, as well as the Department of Defense, stepped up to the challenge and developed environmentally safe

rounds that are still referred to today as “Green Bullets”. Piloted by the Army, the military effort began back in the early 1990s to develop green bullets and was formally introduced for use in 1999. The major difference between the conventional lead bullet used previously and the green bullet developed by the Army was the replacement of the lead core with one made of tungsten and nylon surrounded by a copper-jacket (Greenwire, 1999; CBS, 2005). Since tungsten has comparable chemical properties with lead, it was thought at the time to be a suitable substitute that would maintain similar flight characteristics while eliminating additional contamination to the soil and groundwater adjacent to outdoor ranges. Four years after introduction, further research conducted by the Stevens Institute of Technology in Hoboken, New Jersey found tungsten to be soluble and quite capable of transport through soil under certain conditions (CBS, 2005). The record of air sampling studies specific to the Green Bullets manufactured by the Army were not found within the current literature. Acknowledging that this bullet may not have solved the environmental concern in which it was originally intended, the Army continues to research other alternatives that will be safer for both the environment as well as human health.

Faced with similar environmental concerns as well as potential health concerns to instructors and shooters, the Air Force also searched for a suitable lead-free replacement to the conventional bullet (US AFIERA, 1999). A comprehensive study performed in 1999 suggested that lead-free ammunition was less toxic than conventional rounds. Based on these results, the Air Force approved temporary use of lead-free ammunition manufactured by Olin Winchester for a few installations in order to perform further testing. In Mar 2001, the Air Force Institute for Environment, Safety, and Occupational

Health Risk Analysis, Industrial Hygiene (IH) Branch conducted two rigorous studies to evaluate an enclosed and semi-enclosed range during use of frangible lead-free bullets (Culp, 2001a; Culp, 2001b). A frangible round will “break apart into smaller fragments when impacted with any surface harder than its own.” and is designed to prevent the bullet from ricocheting off a surface back toward the shooter or any other innocent bystander in the area (Mullins, 2001). At the time, both ranges were firing Olin Winchester Ranger Law Enforcement ammunition during M16 rifle and M9 pistol training. Constituents making up the different components of these specific bullets are summarized in Table 2.3.

In the original study performed by AFIERA at Randolph Air Force Base, Texas, the IH Branch sampled for copper, lead, nickel, zinc and tungsten. At the time of sampling, five shooters fired 80 rounds each for a total of 400 rounds. Due to the size of the range, the maximum number of students able to fire at one time was seven. Five air samples were taken behind the firing line for each metal of interest during M16 training; two personal breathing zone samples and three area samples. Results found all metal concentrations to be well below their OEL with the exception of copper. Concentrations for copper were found to be less than 34% of the OEL and less than 3.4% of the PEL for fumes and dust, respectively. Based on additional information provided by the local Bioenvironmental Engineering Flight as well as interviews with range instructors, this evaluation also documented students experiencing headaches during firing operation as well as an excess of visible unburned propellant accumulating on the range floor. Concerns generated in this study lead to an additional study being performed at Columbus AFB in Missouri.

Table 2.3 Chemical Composition of Olin Winchester Frangible Ammunition
(Culp, 2001a)

<i>Component</i>	<i>Constituents</i>
Bullet	Tungsten powder (CAS #7440-33-7)* Copper powder (CAS #7440-50-8)* Nylon (CAS # is proprietary)* Zinc stearate (CAS #557-05-1), <8% Additives (proprietary), <2%
Shellcases and primer cup	Copper (CAS #7440-50-8), 61-96% Lead (CAS #7439-92-1), <0.1% Zinc (CAS #7440-66-6), balance
Primer mix	Diazodinotro phenol (CAS #4682-03-5), 2-5% Potassium nitrate (CAS #7757-79-1), 3-5% Nitrocellulose (CAS #9004-70-0), 1.5-2.5% Boron metal (CAS #7440-42-8), 0.5-1.5% Nitroglycerin (CAS #55-63-0), 0.1-0.5% Tetrazene (CAS #109-27-3), 0.5-1% Nickel (CAS #7440-02-0), 0.03-0.06%
Propellant	Nitroglycerin (CAS #55-63-0), 0-40% Dibutyl phthalate (CAS #84-74-2), 0-10% Polyester adipate (proprietary), 0-10% Ethyl centralite (CAS #85-98-3), 0-10% Rosin (CAS #8050-09-7), 0-5% Ethyl acetate (CAS #141-78-6), 0-1.5% Diphenylamine (CAS #122-39-4), 0.3-1.5% N-Nitroso diphenylamine (CAS #86-30-6), 0-1.5% Potassium nitrate (CAS #7778-80-5), 0-1.5% Potassium sulfate (CAS #7778-80-5), 0-1.5% Tin dioxide (CAS #18282-10-5), 0-1.5% 2-Nitro diphenylamine (CAS #119-75-5), 0-1.5% Graphite (CAS #7782-42-5), 0.02-1% Calcium carbonate (CAS #1317-65-3), 0-1% Nitrocellulose (CAS #9004-70-0), balance
* The manufacturer classifies the percentage range or this component as proprietary.	

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During March 2001, the IH Branch conducted a similar evaluation at the enclosed range located on Columbus Air Force Base MS (Culp, 2001b). In addition to the metals sampling collected at Randolph Air Force Base, there was a closer examination of combustion products created during firing operations. These contaminants were likely to have caused the eye and nose irritation identified in the

previous study. Since nylon was one of the main constituents of the bullets being fired, a particular interest was given to its associated by-products; specifically hydrogen cyanide and ammonia gas. The sampling strategy at this range included four area samples for metals, hydrogen cyanide, and ammonia gas located at various locations throughout the range as well as one personal breathing zone sample for hydrogen cyanide and ammonia gas. Similar to the results found at Randolph Air Force Base, metal concentrations found at the range were less than half of their OEL with the exception of copper. During this round of sampling, copper was found to reach 8.5% of the copper dust PEL and up to 85% of the copper fume OEL. To date, there is no approved sampling method available to distinguish the exposures attributed between copper dust and fumes; both are collected on a mixed cellulose ester filter. Information provided by Olin Winchester however indicated that the “gases resulting from this burning propellant can reach temperatures over 4941 degrees Fahrenheit” (Culp, 2001b). Since the boiling point of copper is 4703 degrees Fahrenheit, it is likely that copper concentrations could be in either the form of copper fumes or copper dust. Using a dust to fumes ratio, this study indicated that comparison to the dust standard would be more representative of true worker exposure.

In accordance with the Air Force Civil Engineering Support Agency (AFCESA), Engineering Technical Letter (ETL) 02-11, “special non-toxic training ammunition” was permitted in 2002 to reduce the cost required to fix an existing ventilation system as long as the ammunition was MAJCOM approved (Department of the Air Force, 2002). In June 2002, the Air Force Center for Environmental Excellence approved the Air Force to fire “Reduced Hazard Frangible Ammunition, 5.56 mm caliber, National Stock Number

(NSN) 1305-01 463-8232, manufactured by Winchester ammunition” (HQ Air Force Center for Environmental Excellence, June 2002) for training purposes. Since that time, AFCESA has revised its Engineering Technical Letter to read as follows, “lead-free ammunition is now available and may be used to eliminate contamination concern with older existing ventilation systems” (Department of the Air Force, 2005)

Based on information collected from Combat Arms Training and Maintenance (CATM) shops across the Air Force, other types of lead-free frangible ammunition are now being utilized. Lead-free bullets used within the Air Force now include the Frangible Non-toxic Ammunition manufactured by Olin Winchester and Ballisticlean ammunition manufactured by the Federal Cartridge Company. Chemical compounds of potential concern in the authorized bullets include tin, copper, zinc, barium, aluminum as well as the by-products associated with nylon and combustion. See Table 2.4 for a summary of the associated health effect associated with the analytes of interest.

Like lead, OSHA, NIOSH, and the ACGIH have also established limits for the components and by-products associated with the frangible lead-free ammunition designed to protect human health. Table 2.5 lists exposure limits for compounds and by-products associated with the lead-free ammunition currently being used by the Air Force. In addition to the public health services, the EPA has also established National Ambient Air Quality Standards for nitrogen dioxide and carbon monoxide as directed by the Clean Air Act (U.S. EPA, 2005). The nitrogen dioxide standard of $1.2 \mu\text{g}/\text{m}^3$ is averaged over a year period while the limits established for carbon monoxide of 9 parts per million (ppm) and 35 ppm are averaged over an 8-hour and 1-hour averaging time respectively. Toxicology information for these analytes is discussed in section 2.5.

Table 2.4 Associated Health Effects of Analytes of Interest (USDHHS, 1997)

Chemical	Health Hazard		Target Organs
	Route *	Symptoms	
Lead	Inhalation	Weakness, tremors, exhaustion, abdominal pain, kidney disease, eye irritation, paleness, anemia, pale face, gingival lead line	Eyes, GI tract, CNS, kidneys, blood, gingival tissue
	Ingestion		
	Contact		
Copper (dust / fumes)	Inhalation	Irritation of eyes, nose, pharynx, upper respiratory; nasal perforation, metallic taste	Eyes, skin, respiratory system, liver, kidneys (increased with Wilson's disease)
	Ingestion		
	Contact		
Tin	Inhalation	Irritation of eyes, skin, respiratory system	Eyes, skin, respiratory system
	Contact		
Aluminum	Inhalation	Irritation of eyes, skin, respiratory system	Eyes, skin, respiratory system
	Ingestion		
	Contact		
Barium Nitrate (as Barium)	Inhalation	Irritation of eyes, skin, upper respiratory system; cough, slow pulse, stomach inflammation	Eyes, skin, respiratory system, heart, CNS
	Ingestion		
	Contact		
Zinc (as Zinc Oxide)	Inhalation	Metal fume fever, chills, muscle ache, fever, dry throat, cough, metallic taste, blurred vision, tight chest, restricted lungs	Respiratory system
Ammonia	Inhalation	Irritation of eyes, nose, throat; breathing difficulty, chest pain, pulmonary edema	Eyes, skin, respiratory system
	Ingestion		
	Contact		
Hydrogen Cyanide	Inhalation	Asphyxia, weak, headache, confusion, nausea, vomit, increased rate of respiration	CNS, Cardiovascular system, thyroid, blood
	Ingestion		
	Contact		
Nitric Oxide	Inhalation	Irritation of eyes, wet skin, nose, throat; drowsiness, blood disorder, unconsciousness	Eyes, skin, respiratory system, blood, CNS
	Ingestion		
	Contact		
Nitrogen Dioxide	Inhalation	Irritation of eyes, nose, throat; cough, chest pain, decreased pulmonary function/edema, rapid heart beat	Eyes, skin, respiratory system, Cardiovascular
	Ingestion		
	Contact		
* Column lists toxicologically important routes of exposure			

Table 2.5 Exposure Limits for Compounds Associated with Lead-Free Frangible Ammunition Currently Being Used by the Air Force (USDHHS, 1997; ACGIH, 2002; U.S. EPA, 2005)

Chemical	OSHA (PEL)		NIOSH			ACGIH (TLV)	
	8-Hour TWA mg/m ³	15 min STEL mg/m ³	10-Hour TWA mg/m ³	STEL mg/m ³	IDLH mg/m ³	8-Hour TWA mg/m ³	STEL mg/m ³
Copper (dust)	1	-	1	-	100 (as Cu)	1	-
Copper (fumes)	0.1	-	0.1	-	100 (as Cu)	0.2	-
Tin	2	-	2	-	100 (as Sn)	2	-
Aluminum	10	-	5	-	N.D.	10	-
Barium Nitrate (as Barium)	0.5	-	0.5	-	50 (as Ba)	0.5	-
Zinc (as Zinc Oxide) (fumes)	5	-	5	10	500	5	10
Zinc (as Zinc Oxide) (dust)	15	-	5	Ceiling 15	500	10	-
Ammonia	34.8	-	17.4	24.3	209	17.4	24.4
Hydrogen Cyanide	11.1	-	-	5.2	55.2	-	Ceiling 5
Nitric Oxide	30.7	-	30.7	-	122.7	30.7	-
Nitrogen Dioxide	-	Ceiling 9.4	-	1.9	37.6	5.6	9.4
Carbon Monoxide	50 ppm	-	35 ppm	Ceiling 200 ppm	1200 ppm	25 ppm	-
PEL = Permissible Exposure Limit							
STEL = Short Term Exposure Limit							
Ceiling = at no time should this limit be exceeded							
N.D. = IDLH has not yet been determined							
mg/m ³ = milligrams per cubic meter							
ppm = parts per million							

2.6 Toxicology Information

2.6.1 Metals (Inhalation/Ingestion Exposure)

Copper is considered a respiratory irritant. Individuals exposed to copper via inhalation will often show symptoms of coughing, sneezing, runny noses as well as in some cases chest pain (USDHHS, 2004). In 1981, a human study was initiated to evaluate the toxic effects of inhalation exposure associated with copper for roughly 100 individuals engaged in sieving copper. Over a three year period, concentrations of copper exposure ranged from 111 mg/m³ to 434 mg/m³. Workers' chest x-rays showed both thickening and scarring of the lungs. Similar animal studies involving mice being exposed to concentrations of 0.12 mg/m³ of copper as copper sulfate three hours a day, five days a week for two weeks also supported the respiratory effects found in the human study involving copper sieve workers (USDHHS, 2004); specifically thickening of the alveolar tissue. This animal study also noted a positive relationship between concentration and severity. In other words, as the concentrations of copper increased, respiratory effects in the mice also increased. Depending on the cleaning and maintenance practices at various shooting ranges, dust build-up may also lead to exposure through ingestion. Gastrointestinal effects from copper include anorexia, nausea, and occasional diarrhea (USDHHS, 2004). In addition to the stomach and lungs, studies involving copper workers also identified airborne copper exposure to affect the blood, liver and endocrine system. Other effects reported included headaches, vertigo, drowsiness and impotency (Department of Health and Human Service, 2004).

When tin is combined with carbon-containing materials it forms what is known as an organotin compound. These compounds can be used to develop plastics which are

often used to bind together other potentially toxic metals often found in frangible ammunition (Mullins, 2001). Since the metabolism of copper, zinc and other metals are affected by tin, it is very difficult to isolate health effects corresponding specifically to tin (USDHHS, 1992). Although low in toxicity, inhalation exposure to tin in the form of dust can affect human lung tissue over time. In addition to targeting the respiratory system, inorganic tin compounds can also cause dermal and ocular irritation as well as abdominal pains at high concentrations. Other human and animal studies suggest exposure to tin can also target the liver, kidney as well as the blood (USDHHS, 1992). No carcinogenic effects associated with inhalation exposure to inorganic tin or organotin compounds have been documented by the Agency of Toxic Substance and Disease Registry (USDHHS, 1992).

Respiratory and neurological effects have been strongly associated with occupational workers being exposed to aluminum. Aluminum welders and iron welders working on railroad tracks were compared in one study to identify a dose response relationship between inhalation exposure to aluminum fumes and specific health effects (World Health Organization, 1997). Occupational welders working with aluminum for 13 years were found to have minor neuropathy and in some cases degradation of brain function. Two independent studies conducted during aluminum manufacturing and soldering operations involving potassium aluminum tetrafluoride flux found reports of “irritant induced asthma” to be directly associated with inhalation exposure to aluminum (World Health Organization, 1997). Finally, nine other documented cases of interstitial fibrosis were linked to chronic inhalation exposure to aluminum oxide.

Human studies suggest little to no effect on the respiratory system from chronic exposure to barium (USDHHS, 1992). Another study involving chronic exposure to barium carbonate dust did however show instances of elevated blood pressures and heart irregularities (USDHHS, 1992). An animal study involving guinea pigs documented in 1986 showed similar cardiovascular effects (USDHHS, 1992). In a final study, accidental over exposure to large concentrations of barium also suggested causality of abdominal cramps, nausea, as well as muscle weakness and kidney failure (USDHHS, 1992).

The health effects associated with zinc inhalation exposure comes primarily from zinc oxide. Respiratory symptoms associated with acute exposure to low concentrations of zinc oxide may include coughing and dryness of the throat (USDHHS, 1994). At high concentrations ranging from 320 mg/m³ to 580 mg/m³, individuals will experience chest pains and breathing difficulties often referred to as metal fume fever. Although symptoms may cease within as little as 4 days, ultra fine zinc oxide particles that are less than one micrometer in diameter may travel to the alveoli and initiate irritation as well as damage to the lining of the lung. In addition, individuals being exposed to high concentrations may experience fever, headache and depression (U.S. Department of Human Health and Human Services, 1994).

2.6.2 Nylon By-Products (Inhalation Exposure)

At concentrations exceeding 30 ppm (21 mg/m³), ammonia can quickly lead to nose and throat irritation (USDHHS, 2004). Occupational studies conducted within enclosed buildings and fertilizer factories have shown a strong association between ammonia gas and respiratory disorders. Individuals exposed over the ACGIH 8-hr TLV-TWA of 25

ppm were found to have an elevated risk of experiencing wheezing, coughing and asthma relative to those exposed below the standard (USDHHS, 2004). Another human study specific to soda ash factory workers found that long term exposure to concentrations averaging 12.5 ppm had no significant effects on pulmonary function or odor sensitivity (USDHHS, 2004). In addition to potential respiratory difficulties, animal studies suggest both acute and chronic exposure to ammonia can decrease the resistance to bacterial infection and decrease immune response to infection (USDHHS, 2004).

Short term inhalation exposure to low concentrations of hydrogen cyanide have been found to cause numerous symptoms associated with the central nervous system to include lightheadness, breathlessness, dizziness, numbness as well as headaches (USDHHS, 1997). Humans exposed up to 15 ppm (16.6 mg/m³) of hydrogen cyanide for unspecified durations reported signs of sleep disruption, fatigue, ringing in their ears, skin sensation of extremities and in some cases loss of consciousness in addition to those symptoms mentioned previously (USDHHS, 1997). Animal studies involving dogs being exposed to hydrogen cyanide concentration of 45 ppm for various durations ranging from 28 to 96 days were found to cause tremors, convulsions and comas (USDHHS, 1997).

In addition to problems associated with the central nervous system, the previously mentioned human study also has shown hydrogen cyanide to affect the human cardiovascular and endocrine systems (USDHHS, September, 1997). Individuals working in the silver plating facility exposed to 15 ppm of hydrogen cyanide were also found to experience instances of palpitations and chest pains; the percentage of workers experiencing these conditions were 14% and 31% respectively. An additional finding from this study showed significantly higher thyroid stimulating hormone levels in

workers exposed to 15 ppm (USDHHS, September, 1997). High thyroid stimulating hormones (above 4.5 milli-international units per liter for adults) can lead to thyroid failure and may ultimately affect all body functions (Nissl, 2004). While the hydrogen cyanide level depicted in this study was higher than the OSHA PEL of 10 ppm, extreme airborne concentrations of hydrogen cyanide (546 ppm) have been shown to cause death in roughly 10 minutes.

Other by-products associated with nylon include nitrogen oxides. The Agency of Toxic Substances and Disease Registry recognizes nitric oxide and nitrogen dioxide as the most toxicologically significant of these nitrogen and oxygen mixtures (USDHHS, 2002). At low levels, nitrogen oxides act as an irritant. It primarily affects the nose, eyes and throat and can lead to respiratory problems. Some symptoms experienced include fatigue, nausea and breathing difficulties. In some instances, individuals exposed to nitrogen oxides may also experience fluid build-up in the lungs in as little as 2 days of exposure. At higher concentrations, a more severe affect on the throat and lungs may occur including burning and tissue swelling.

2.7 Methods

In order to determine if individuals are over the exposure standards outlined in section 2.5, air samples must be collected and analyzed in a standardized reliable manner. NIOSH, OSHA and EPA have validated specific methodologies outlining the proper sampling protocol, media, minimum and maximum flow rates and volumes as well as the measurement techniques needed to perform an analysis for a specific compound. While the EPA has developed some reference methods to monitor ambient air quality for carbon monoxide and nitrogen dioxide, OSHA and NIOSH have established detailed sampling

methods for all of the components and by-products associated with the lead-free bullets currently being used by the Air Force. Table 2.6 lists the specific methods developed by NIOSH and OSHA. A detailed description of the specific methodology used within the scope of this research is further discussed in Chapter III.

Table 2.6 OSHA and NIOSH Ambient Air Sampling Methods

Chemical	Methods	
	OSHA	NIOSH
Copper	ID121	7300
Tin	ID121	7300
Aluminum	ID121	7300
Barium Nitrate (as Barium)	ID121	7300
Zinc (as Zinc Oxide) (dust/fumes)	ID121	7300
Ammonia	ID188	S347
Hydrogen Cyanide	ID120	6010
Nitric Oxide	ID190	6014
Nitrogen Dioxide	ID182	6014

2.8 Summary

Use of conventional ammunition at indoor and outdoor small arms shooting ranges places instructors and shooters at risk of airborne lead exposure. Overexposure to lead can cause adverse health effects which target a wide variety of organs and systems within the human body. Lead concentrations at shooting ranges can be reduced significantly by implementing best management practices and the use of jacketed

ammunition, however, the only way to eliminate all health effects associated with lead is to eliminate this toxic metal altogether.

Since the substitution of leaded ammunition with lead-free bullets has been shown to eliminate potential airborne lead exposure to instructors and shooters, it is now important to shift attention to the materials selected by manufacturers to replace lead. In industry, it is not uncommon to replace one toxic material known to cause adverse health effects to humans with another with little to no toxicity data associated with it. With more and more Air Force shooting ranges using these frangible lead-free bullets, it is imperative to determine that manufactures have not merely substituted a bullet that is just as toxic as or more toxic than the original ammunition. The methodology and analysis presented in chapter III and IV will broach this subject and bring industrial hygienists one step closer to determining if range instructors and shooters across the Air Force are at risk of exposure from the materials and by-products associated with lead-free ammunition during M16 qualification firing operations.

III. Methodology

This chapter illustrates the methodology used to address the research of the following questions originally outlined in Chapter I.

(1) How many bases have transitioned to lead-free ammunition? What is the maximum and average lead exposure during small arms qualification training using both lead and lead-free bullets? How much is lead exposure reduced through the use of lead-free bullets?

(2) What other potential airborne chemical exposures have been introduced to Air Force instructors and shooters during small arms weapon qualification training as a result of the transition to Green Bullets?

The chapter also discusses the approach taken to gather firing range design information and historical lead air sampling results. It further describes the sampling strategy used at two Air Force installations selected to take part in a comprehensive evaluation designed to identify and quantify representative airborne exposures to instructors associated with frangible lead-free bullets. Furthermore, it describes a parallel lead-free ammunition study at two additional bases being conducted by the Air Force Research laboratory (AFIOH) at Brooks AFB, TX and the collaborative effort being made with the author. Finally, this chapter discusses the type of media and flow rate ranges used, in accordance with specific NIOSH methods, to sample and analyze specific analytes of interest as well as the approach taken to screen for carbon monoxide during M16 firing operations.

3.1 Historical Data Call

A data call request was developed to gather information on the current firing range designs for Air Force bases located across the United States. Data requested included types of 5.56 mm ammunition being fired, types of bullet traps currently being used, the physical location of the firing and whether the weapons firing operations took place inside or outside. In addition to the specific descriptive information for each base's current firing range configuration, historical personal and area air sampling results for M16 rifle firing were also requested to determine past personnel exposures from conventional lead bullets. The historical data request form is shown in Appendix B. Once constructed, the data request was reviewed by the Human Subjects Board and approved for distribution on 20 July 2005 (Department of the Air Force, 2005). A census of 63 active duty CONUS bases making up 6 Major Commands was attempted. Major Commands queried included Air Combat Command (ACC), Air Education and Training Command (AETC), Air Force Material Command (AFMC), Air Force Space Command (AFSPC), Air Force Special Operations Command (AFSOC), and Air Mobility Command (AMC). The Board approval letter is shown in Appendix B.

In order to receive maximum support, distribution of the historical data request forms was routed through the Command Bioenvironmental Engineers. The Command Bioenvironmental Engineers were briefed on the background and scope of work to be performed and then asked to forward the data call request, accompanied by their supporting remarks, to their respective Bioenvironmental Engineering (BEE) Flight Commanders. A one-month suspense was given to each Flight Commander to compile and submit their responses directly to AFIT. Follow-up telephone calls and e-mail

requests, to combat non-response errors, were then made directly to each base to ensure bases had an adequate opportunity to participate in the data call. Roughly 25% of the bases responded with the information requested. See Appendix B for a summary of participating bases and associated responses. In order to include as much of the sample population as possible, air sampling results were also extracted through the Command Core System (CCS) Warehouse located at Brooks AFB, Texas with the assistance of Mr. Tom Hewitt (Hewitt, Sep 2005). The CCS warehouse is a database originated to serve as a repository of information on specific activities performed and evaluated during BEE routine and special surveillance. Air Force bases both stateside and abroad may use this database at anytime to review results and findings for similar operations currently being investigated. By utilizing this additional source of information, lead air sampling results were obtained for 60% of the bases originally polled. Follow-up telephone calls were then made to BEE flights and CATM range instructors at specific locations to inquire about information on the type of range, bullets, and traps being used to help categorize air sampling results taken from the CCS.

3.2 Analytes of Concern

The majority of bases performing M16, 5.56 mm, firing operations are now using frangible ammunition with a National Stock Number (NSN) of 1305-01-463-8232; specifically Frangible Non-toxic Ammunition, manufactured by Olin Winchester, or Ballisticlean ammunition, manufactured by the Federal Cartridge Company. A variety of frangible bullet types are being sold by these companies. Therefore, specific nomenclatures for the bullets found at firing ranges were confirmed by contacting the manufacturer directly; to verify specific ammunition in use based on lot numbers.

Components of each type of frangible ammunition being fired were then identified using the Material Safety Data Sheets found in Appendix C. Chemical compounds of concern included tin, copper, zinc, barium, aluminum, and Zytel nylon. Of particular concern are the byproducts, ammonia and hydrogen cyanide, associated with the Zytel nylon that are formed as the bullet is fired.

3.3 Data Collection

Air sampling was conducted at two facilities, Hill AFB and McGuire AFB by the author. Collaboration was also completed with the Air Force Institute for Operational Health with sampling results obtained from Ellsworth, Offutt, and Whiteman AFB. Virtually the same data was collected by the author and AFIOH personnel, at the respective bases.

3.3.1 Hill AFB

The indoor firing range (Building 741) at Hill AFB, UT is completely enclosed with unpainted concrete walls on both sides of the range as well as a concrete, unpainted floor. While the area between the firing line and the hard bullet trap down range is covered by metal overhead baffles, the area up range from the firing line has been finished with the addition of a false ceiling. Ventilation for the range was provided through the use of a supplied air wall located up range from the shooters and instructors. Figure 3.1 illustrates the supplied air wall used during firing operations.

Air sampling was conducted at the indoor small arms firing range on the 21st and 23rd of September 2005 to capture representative range instructor's chemical airborne exposures during M16 Air Force Qualification Training. Three instructors were selected during each respective class to represent unique exposures of individuals typically

located in specific areas of the range. Instructors were chosen for monitoring as they are the individuals who are exposed day-after-day to contaminants found at the range. Shooters are considered to be only intermittently exposed to contaminants generated during firing operations. Figure 3.2 illustrates the specific areas in which the instructors concentrated their time during weapon qualification training. Two firing line instructors performed their duties primarily between the firing line and ready line while the command (tower) instructor was centered at the back of the range, roughly 13 feet behind the firing line, elevated on a platform about two and half feet above the floor.



Figure 3.1 Supplied Air Wall. Air movement designed to force air contaminants down range away from instructors and shooters.

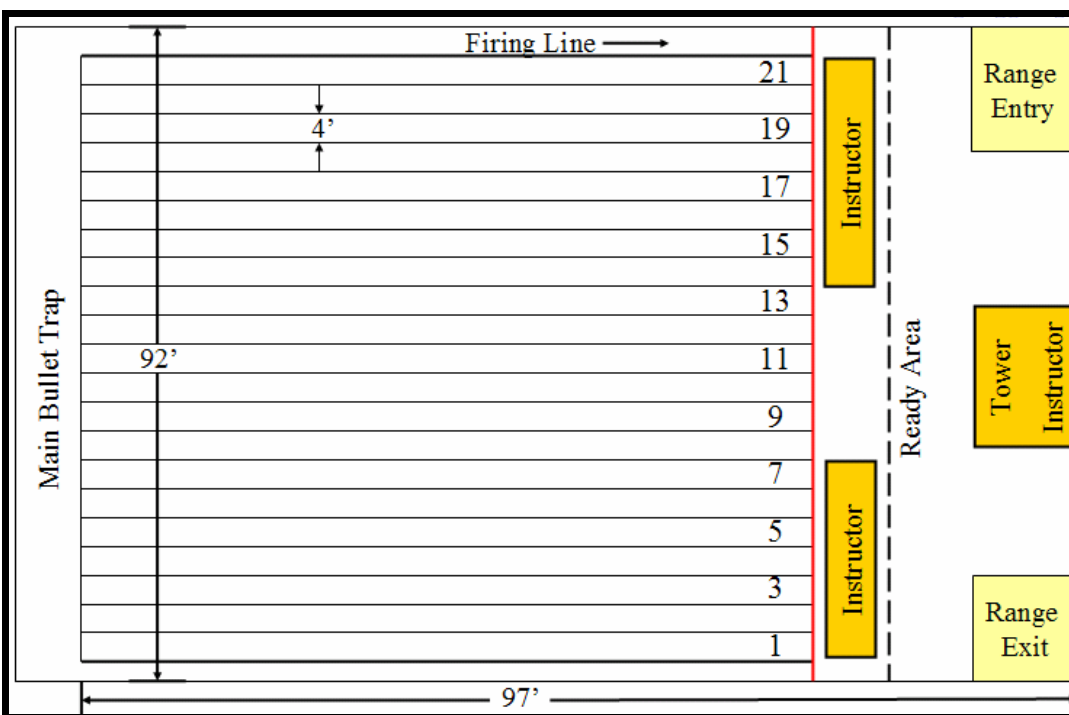


Figure 3.2 Plan View of Hill AFB CATM Range. Three instructors were monitored for chemical exposures.

Each individual being monitored was equipped with three air sampling pumps (Gilian, Florida; SKC, Pennsylvania) to collect personal air samples representative of instructors' inhalation exposure. Pumps were connected via Tygon tubing to either a 37-mm filter cassette or adsorbent charcoal tube positioned in the breathing zone as shown in Figure 3.3. Samples collected were analyzed using NIOSH method 7300 for specific metals of interest previously mentioned in Table 2.4 and NIOSH method 6010 and S347 for by-products (hydrogen cyanide and ammonia respectively) associated with the nylon used in the frangible rounds.



Figure 3.3 Personal Air Sampling Assembly to Capture Breathing Zone Contaminants

Required media, average flow ranges and volumes for specific NIOSH methods are summarized in Table 3.2. Table 3.2 specifies the main analyte, the sampling method, the sampling media (what the analyte is collected upon), the analytical chemical technique used, the flow rate of the air sampling pump, and the minimum volume of air required for collection. The specific analytical protocol for each method is outlined in section 3.4.

In addition to air sampling, a direct reading indoor air monitor, TSI Q-TRAK Model No. 8551 (TSI, Minnesota), was used to determine minimum, maximum, and average carbon monoxide levels during shooting operations. The monitor was positioned behind a shooting barricade, as illustrated in Figure 3.4, between two students (stations 8 and 14 in the Figure 3.2)

Table 3.2 Sampling Specifications for Analytes of Interest

Substance ¹	Sampling Method	Sampling Media	Measurement Technique	Flow Rate (LPM)	Sampling Volume (L)
Copper (Dust & Fume)	NIOSH 7300	0.8 um cellulose ester membrane	Inductively coupled Argon Plasma - Atomic emission spectroscopy	1 - 4	5 – 1000
Zinc	NIOSH 7300	0.8 um cellulose ester membrane	Inductively coupled Argon Plasma - Atomic emission spectroscopy	1 - 4	5 – 200
Tin	NIOSH 7300	0.8 um cellulose ester membrane	Inductively coupled Argon Plasma - Atomic emission spectroscopy	1 - 4	5 – 1000
Lead	NIOSH 7300	0.8 um cellulose ester membrane	Inductively coupled Argon Plasma - Atomic emission spectroscopy	1 - 4	50 – 2000
Ammonia	NIOSH S347	Solid sorbent tube (sulfuric acid-treated silica gel)	Ion Chromatograph, Conductivity Detection	0.1 - 0.5	0.1 – 96
Hydrogen Cyanide	NIOSH 6010	Solid sorbent tube (soda lime, 600 mg / 200 mg)	Spectrophotometry, Visible adsorption	0.05 - 0.2	2 – 90
¹ Information obtained from the NIOSH Manual of Analytical Methods					

approximately four and a half feet above the ground to give a general indication of the carbon monoxide levels generated during firing operations. On the 21st of September, 19 shooters participated in the weapons qualification class. Each individual fired 100 rounds for a total of 1900 rounds. Fifteen shooters fired the M16 on the 23rd of September totaling 1500 rounds.



Figure 3.4 TSI Q-TRAK monitoring position. The CO monitor was positioned at station 8 on 21 Sep 05 and station 12 on 23 Sep 05 between two students to monitor CO levels during firing.

3.3.2 McGuire AFB

The outdoor firing range (25A, Rolling Thunder) at McGuire AFB is completely open to the environment. Earth mounds are positioned on both sides of the range as well as behind the down range targets. The floor between the ready line and the earth berm down range consists of sand and loose dirt. The only source of air movement at the range is provided by natural ventilation from prevailing winds. During firing operations, there is a posted flag up range from the firing line used to determine wind direction. Figure 3.5 illustrates the range configuration.

Air sampling was conducted at the McGuire AFB, NJ outdoor small arms firing range on the 2nd and 3rd of November 2005 to capture representative chemical airborne exposures to range instructors during M16 Air Force Qualification Training. Three

instructors were selected during each respective class to represent unique exposures of individuals typically located in specific areas of the range. Figure 3.5 also illustrates the specific areas where these instructors concentrated their time during weapons qualification training. Two firing line instructors performed their duties primarily between the firing line and ready line while the command instructor sat on the mobile command post (tailgate of the bread truck) located 21 feet behind the ready line. Each individual being monitored was equipped with three air sampling pumps (Gilian, Florida; SKC, Pennsylvania) to collect personal air samples representative of their inhalation exposure. Samples collected were analyzed using NIOSH method 7300 for metals and NIOSH method 6010 and S347 for by-products associated with the nylon used in the frangible rounds. Required media, average flow ranges and volumes for specific NIOSH methods previously mentioned are summarized in Table 3.2 with the specific analytical protocols outlined for each method in section 3.4. On the 2nd and 3rd of November, 14 shooters participated in each of the weapons qualification classes. Each individual fired 100 rounds for a total 1400 rounds per qualification session. Since environmental conditions were relatively dynamic due to an outdoor venue, wind direction and wind speeds were also recorded during firing operations for background site information. A TSI ALNOR Compuflow (TSI, Minnesota) Model No. 8585 velometer, Natural Resource Management Area map, and flag were used to measure wind direction and speed. No carbon monoxide sampling was conducted during this survey due to a lack of available equipment.

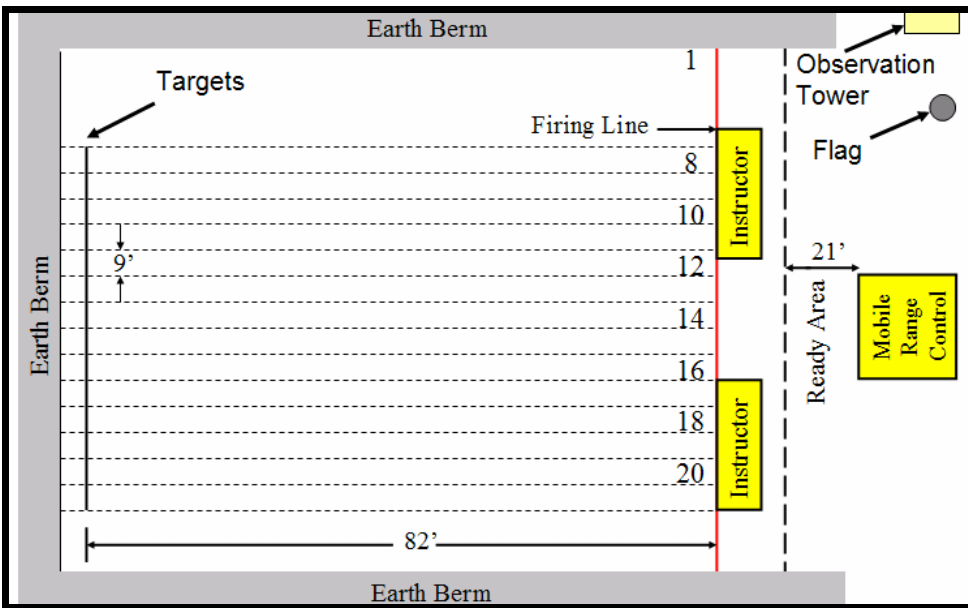


Figure 3.5 Plan View of McGuire AFB CATM Outdoor Range. Two instructors moved between the firing line and the ready line and the third remained near the area marked mobile range control.

3.3.3 AFIOH Collaboration

A parallel study of airborne exposures associated with frangible bullets is currently being conducted by the Industrial Hygiene (IH) Branch of the Air Force Institute for Operational Health (AFIOH) in response to a Headquarters ACC request. After consulting Major Gary Wright, AFIOH Senior Industrial Hygiene Consultant, a collaborative effort was made to share air sampling results and findings associated with hazardous material exposures during the firing of 5.56 mm frangible ammunition. Evaluations of small arms firing ranges performed by the IH Branch of AFIOH included Ellsworth AFB, SD, Whiteman AFB, MO, and Offutt AFB, NE.

The sampling strategy used by the IH Branch of AFIOH mirrored that used by the author with two exceptions (by-products of plastics as well as nitrogen oxides

resulting from the combustion of nylon). Since nylon and plastics are commonly used to bind with metals such as copper, to form the projectile component of lead-free ammunition, the IH Branch of AFIOH also sampled for common by-products of plastics to include hydrogen chloride and phosgene within their study. Additional analytes were not sampled by the author since the material, Zytel nylon, used to bind the copper in the Federal Cartridge Company frangible ammunition fired at Hill AFB and McGuire AFB was clearly identified on the MSDS. Sampling for additional by-products associated with nylon (nitric oxide and nitrogen dioxide) was also not conducted by the author. This choice was made due to limited equipment and the relatively low severity of potential adverse health effects associated at low concentrations in comparison to that of ammonia and hydrogen cyanide (USDHHS, 2002).

3.3.3.1 Ellsworth AFB

The outdoor firing range (Range C) at Ellsworth AFB is semi-enclosed with baffled, unpainted concrete walls on both sides of the range as well as a concrete, unpainted floor. The area between the firing line and the bullet trap down range is covered by metal overhead baffles. No ventilation system was present during the course of this assessment. Wind direction and wind speed were recorded during firing operations as background site information.

Air sampling was conducted at the Ellsworth AFB, SD outdoor small arms firing range on the 23rd of August 2005 to capture representative chemical airborne exposures to range instructors during M16 Air Force Qualification Training. Two instructors were selected to represent exposures of individuals typically performing instructor duties at the range during weapons qualification training. One instructor was located primarily

between the firing line and ready line (stations 14-20) while the command (tower) instructor addressed the students sitting down at the back center of the range. Each individual being monitored was equipped with air sampling pumps (SKC, Pennsylvania) to collect personal air samples representative of their inhalation exposure. On the 23rd of August, 20 shooters participated in the weapons qualification class. Each individual fired 100 rounds for a total of 2000 rounds.

Samples collected were analyzed using NIOSH method 7300 for specific metals identified on the MSDS and NIOSH method 6010, S347, 7903, 6014, and OSHA method 61 for by-products associated with the plastics used in the lead-free frangible rounds (5.56 mm frangible bullets manufactured by Olin Winchester) fired at Ellsworth AFB. Required media, average flow rates and analytes collected are summarized in Table 2 of the Consultative Letter, IOH-RS-BR-CL-2005-xxxx Air Sampling in a Partially Enclosed Firing Range during Use of Frangible Bullets, Ellsworth AFB, SD. Results and findings from this consultative letter can be found in Appendix D-1. No carbon monoxide sampling was conducted during this survey.

3.3.3.2 Whiteman AFB

The outdoor firing range at Whiteman AFB is partially enclosed with baffled, unpainted concrete walls on both sides of the range as well as a concrete, unpainted floor. The area between the firing line and the bullet trap down range is covered by metal overhead baffles. No ventilation system was present during the course of this assessment. Wind direction and wind speed were recorded during firing operations for background site information.

Air sampling was conducted at the Whiteman AFB, MO outdoor small arms firing range on the 13th and 14th of September 2005 to capture representative chemical airborne exposures to range instructors during M16 Air Force Qualification Training. Three instructors on the first day of sampling and two instructors on the second day of sampling were selected to represent unique exposures of individuals typically performing instructor duties at the range during weapons qualification training. Instructors were located primarily between the firing line and ready line while the command (tower) instructor addressed the students sitting down at the back center of the range. Each individual being monitored was equipped with air sampling pumps (SKC, Pennsylvania) to collect personal air samples representative of their inhalation exposure. In addition to personal samples taken on the second day of shooting, one area sample was also taken in a vacant firing position adjacent to shooters on the firing line to capture breathing zone samples for the shooter while in the prone position. On the 13th of September, 20 shooters participated in the weapons qualification class. Each individual fired 100 rounds for a total of 2000 rounds. On the 14th of September, nine shooters fired the M16 rifle during weapons qualification for a total of 900 rounds fired.

Samples collected were analyzed using NIOSH method 7300 for specific metals identified on the MSDS and NIOSH method 6010, S347, 7903, 6014, and OSHA method 61 for by-products associated with the plastics used in the lead-free frangible rounds (Ballisticlean 5.56 mm Centerfire Rifle Ammunition, Federal Cartridge Company) fired at Whiteman AFB. Required media, average flow rates and analytes collected are summarized in Table 3 of the Consultative Letter, IOH-RS-BR-CL-2005-xxxx Air Sampling in a Partially Enclosed Firing Range during Use of Frangible Bullets,

Whiteman AFB, MO. Results and findings from this consultative letter can be found in Appendix D-2. No carbon monoxide sampling was conducted during this survey.

3.3.3.3 Offutt AFB

The outdoor firing range at Offutt AFB is fully enclosed with baffled, unpainted concrete walls on both sides of the range as well as a concrete, unpainted floor. The area between the firing line and the bullet trap down range is covered by metal overhead baffles. No ventilation system was present during the course of this assessment. Wind direction and wind speed were recorded during firing operations for background site information.

Air sampling was conducted at the Offutt AFB, NE outdoor small arms firing range on the 7th and 9th of November 2005 to capture representative chemical airborne exposures to range instructors during M-4 Air Force Qualification Training. The M-4 rifle is comparable to the M16 rifle with the exception of a shorter barrel. One instructor on the first day of sampling and two instructors on the second day of sampling were selected to represent unique exposures of individuals typically performing instructor duties at the range during weapons qualification training. Representative exposure of the command (tower) instructor, located at the back center of the range, was not captured during this assessment. Instructors participating in sampling activities were located primarily between the firing line and ready line. Each individual being monitored was equipped with air sampling pumps (SKC, Pennsylvania) to collect personal air samples representative of their inhalation exposure. In addition to personal samples, three area samples were also taken on each day of firing in vacant firing positions between shooters on the firing line to capture breathing zone samples for the shooter while in the prone

position. On the 7th of November, 7 shooters participated in the weapons qualification class. Each individual fired 100 rounds for a total of 700 rounds. On the 9th of November, 10 shooters fired the M-4 during weapons qualification for a total of 1000 rounds fired.

Samples collected were analyzed using NIOSH method 7300 for specific metals identified on the MSDS and NIOSH method 6010, S347, 7903, 6014, and OSHA method 61 for by-products associated with the plastics used in the lead-free frangible rounds (Ballisticlean 5.56 mm Centerfire Rifle Ammunition, Federal Cartridge Company) fired at Offutt AFB. Required media, average flow rates and analytes collected are summarized in Table 3 of the Consultative Letter, IOH-RS-BR-CL-2005-xxxx Air Sampling in a Partially Enclosed Firing Range during Use of Frangible Bullets, Offutt AFB, NE. Results and findings from this consultative letter can be found in Appendix D-3. Air quality monitors and a cascade impactor were also used to measure carbon monoxide, nitrous oxide, and nitrogen dioxide concentration during firing activities.

3.4 Analytical Methods

3.4.1 NIOSH Method 7300 for Elements

NIOSH Method 7300 can be found in its entirety in Appendix F (U.S. Department of Health, Education, and Welfare, 2003). At each of the bases, metal samples were collected on a 0.8 micron cellulose ester membrane preloaded cassette using Gillian High Flow sampling pumps, Model HFS-513A. A list of specific pumps and calibration equipment utilized throughout the sampling collection process is listed in Appendix E. Security Forces instructors at each base visited indicated firing operations last approximately two hours on average. Pump flow rates were calculated and set between

an average standard flow rate of 0.9665 liters per minute (LPM) and 1.339 LPM in order to maximize the sample volume collected without exceeding the carrying capacity of the media outlined within this method. Sampling pumps were both pre- and post-calibrated with a representative sampler inline using the BIOS Dry Cal DC-2 (Butler New Jersey) primary standard to ensure a continuous steady flow rate was maintained throughout the sampling process. Two field blanks were taken on site prior to firing operations. All samples collected for each day of sampling were logged into the Command Core database and then shipped to the Air Force Institute of Operational Health at Brooks City-Base in Texas for analysis.

Inductively coupled argon plasma, atomic emission spectroscopy (ICP-AES) was used to analyze the metal-containing samples. ICP causes the elements of interest to produce a characteristic wavelength specific light which was then converted into an electric signal that could be quantified. Trace metals analyzed included lead, tin, copper, zinc, barium, and aluminum. Although lead is not one of the components in the ammunition currently being fired, it was also included in the analysis, since previously expended lead rounds may still contribute to the instructor and shooters' potential exposure.

3.4.2 NIOSH Method 6010 for Hydrogen Cyanide

NIOSH Method 6010 can be found in its entirety in Appendix A-5 (U.S. Department of Health, Education, and Welfare, 1994). Samples for hydrogen cyanide were collected on a solid sorbent (soda lime) media using GILAIR-5 Tri-mode air sampling pumps (Gilian, Florida) fitted with a constant low flow module. A list of specific pumps and calibration equipment utilized throughout the sampling collection

process is listed in Appendix E. Based on information provided by Security Forces instructors, firing operations take approximately two hours to perform. Pump flow rates were calculated and set between an average standard flow rate of 0.1232 LPM and 0.1774 LPM in order to maximize the sample volume collected without exceeding the carrying capacity of the media outlined within this method. Sampling pumps were both pre- and post-calibrated with a representative sampler inline using the BIOS Dry Cal DC-2 (Butler, New Jersey) primary standard to ensure a continuous steady flow rate was maintained throughout the sampling process. Two sorbent tube field blanks were taken on site prior to firing operations. All samples collected for each day of sampling were logged into the Command Core database and then shipped to the Air Force Institute of Operational Health at Brooks City-Base in Texas for analysis. Visible absorption spectrophotometry was used to detect and quantify the specific concentrations of hydrogen cyanide for each air sample collected. In order to determine the amount of hydrogen cyanide present for a given sample, it must first be desorbed from the tube using deionized-distilled water. By using a prism, light can be broken down into all the colors within the visible spectrum (380 – 750 nanometers). Once this is accomplished, the light can be focused through a narrow open slit directly at the sample of interest. By rotating the prism, the wavelength of light can be adjusted until it matches up with the color absorbed by the sample. The quantity of hydrogen cyanide present in a sample can then be determined by measuring the intensity of the beam of light as it passes through the given sample.

3.4.3 NIOSH Method S347 for Ammonia

NIOSH Method S347 can be found in its entirety in Appendix F-2(U.S. Department of Health, Education, and Welfare, 1979). Samples for ammonia were collected on solid sorbent (sulfuric acid-treated silica gel) media using GILAIR-5 Tri-mode (Gilian, Florida) air sampling pumps fitted with a constant low flow module. A list of specific pumps and calibration equipment utilized throughout the sampling collection process is listed in Appendix E. As described previously, the firing activity takes approximately two hours to perform. Pump flow rates were calculated and set between an average standard flow rate of 0.1240 LPM and 0.613 LPM in order to maximize the sample volume collected without exceeding the carrying capacity of the media outlined within this method. Sampling pumps were both pre- and post-calibrated with a representative sampler inline using the BIOS Dry Cal DC-2 (Butler, New Jersey) primary standard to ensure a continuous steady flow rate was maintained throughout the sampling process. Two sorbent tubes as field blanks were taken on site prior to firing operations. All samples collected for each day of sampling were logged into the Command Core database and then shipped to the Air Force Institute of Operational Health at Brooks City-Base in Texas for analysis. Ion chromatography was used to detect and quantify the specific concentrations of ammonia. Ammonia was desorbed from the tube using 10 ml of 0.1 N sulfuric acid and then broken down into an 8 ml aliquot. Next, the sample was transported through a liquid chromatograph system by a mobile fluid stream. As the ammonia in the mobile stream interacts with the stationary media, it will separate ammonia ions from the solution. Once separated, the ions can be quantified to determine ammonia concentrations.

3.4.4. Carbon Monoxide Monitoring

Carbon monoxide (CO) can be generated as a result of incomplete combustion when firing small arms. A TSI Q-TRAK indoor air quality monitor (TSI, Minnesota) was used at Hill AFB to screen for elevated levels of carbon monoxide during firing operations. By using the logging feature on the instrument, minimum, maximum, and average CO concentration levels were determined for the duration of firing at the indoor range. CO concentration monitoring was only accomplished at Hill AFB due to a lack of equipment at McGuire AFB.

3.5 Summary

A systematic approach was used to identify specific firing range information and collection of representative airborne exposures to Air Force instructors during M16 firing using conventional lead and lead-free frangible bullets. By collecting historical data specific to range configuration and personal airborne exposures during use of conventional lead bullets for all Air Force installations within the CONUS United States, a baseline of instructor exposure was established for future comparison. Analytes of concern identified as components of frangible lead-free bullets being used were then sampled and analyzed using NIOSH methods. Observations as well as results from analysis and direct reading measurements will be discussed in Chapter IV.

IV. Results and Discussion

This chapter discusses the results and findings for the methodology outlined in Chapter III. First, a discussion of the firing range information from the historical data call will be reviewed to give a descriptive overview of range configurations across the Air Force. Air sampling results for lead exposure levels during lead and lead-free firing operations will then be presented to illustrate representative instructor exposures under each specific condition. Procedures used to analyze and compare the results will also be discussed in detail. Finally, results for other chemical constituents evaluated during lead-free firing operations will be examined to identify potential airborne exposures to instructors.

4.1 Descriptive Findings from Data Call Request

Sixty-three active duty base Bioenvironmental Engineering (BEE) Offices were polled in order to determine descriptive firing range information trends across the Air Force. Over 420 air sampling results were compiled and statistically analyzed to determine the average representative instructor airborne exposure during firing of leaded ammunition at both indoor and outdoor firing ranges. The number of samples compiled from indoor ranges and outdoor ranges were 91 and 330, respectively. In addition to specific personal exposure samples collected during M16 firing, four additional samples were also considered to identify additional exposures to instructors accumulated during firing range cleaning and abatement activities.

Once the average representative lead exposures were determined for indoor and outdoor firing ranges, two indoor and four outdoor firing ranges currently firing frangible

lead-free ammunition were randomly selected and visited through a collaborative effort with the Air Force Institute for Operational Health (AFIOH) to assess instructor exposure and current range conditions. The author evaluated firing ranges at Hill AFB and McGuire AFB while AFIOH concentrated their efforts at Ellsworth AFB, Whiteman AFB, and Offutt AFB. In addition to lead-free sampling conducted at these five bases, air sampling results for metals were also included from the indoor firing range at Wright Patterson AFB. The purpose of each site visit was to collect breathing zone samples representative of instructor exposure to determine the relative reduction in lead exposure between firing ranges shooting lead and lead-free ammunition. Additionally, exposures generated from metals and combustion by-products associated with nylon and plastics were evaluated. Air samples collected during M16 firing of frangible lead-free ammunition for six metals and six combustion by-products totaled 241 samples. This section will discuss specific analytical procedure used as well as report results found throughout the course of this research.

An electronic mail data call request was sent through the MAJCOMs to 63 active duty Air Force installation BEE Offices located within the Continental United States (CONUS) to identify Air Force-wide trends regarding key parameters, such as ammunition being fired, types of bullet traps and range configuration at indoor and outdoor shooting ranges. Eighteen offices responded. Information collected from the 18 bases indicated all but two firing ranges have transitioned to some brand of the 5.56 mm lead-free bullets used during M16 firing operations. Over 50% of those bases identified as using lead-free bullets are firing ammunition with a National Stock Number (NSN) of 1305-01-463-8232 manufactured by either Olin Winchester or the Federal Cartridge

Company. Other manufacturers supplying lead-free ammunition under the same NSN to Air Force shooting ranges include Action Target and the Federal Ammunition Company.

Because of limited responses, the Command Core System (CCS) database was then used to extract air sampling data for bases not responding to the initial data call. This secondary resource provided range data for 20 additional CONUS installations. Lead air sampling data from the Command Core warehouse database was first queried using the lead chemical Abstract Service (CAS) number, 7439921. Results for lead air samples collected for all activities conducted within the Air Force were then sorted to separate firing range specific processes from other activities involving lead exposures found within the system. Process categories used to categorize sampling results included variations of the following, “Security Forces”, “Combat Arms Training and Maintenance”, as well as “indoor” and “outdoor” firing ranges. Due to a lack of information in the CCS regarding the range configuration at each installation, BEE Flights and CATM instructors from each base were then contacted by phone to determine whether their range was located inside or outside. Additional information collected through these phone calls mirrored that requested in the original data call to include use of lead and lead-free bullets as well as the general category of bullet traps found at each range. Table 4.1 shows the number of responses by MAJCOM as well as the overall percentage of data collected through the original data call and the CCS system across the Air Force.

Table 4.2 summarizes the breakdown of range information acquired from primary and CCS resources. Results from the data call, CCS and follow-up suggest that the majority of bases across the Air Force have transitioned to alternative lead-free

Table 4.1 Installation Response to Firing Range Data Call by MAJCOM

MAJCOM	Base Responses	Number of Bases	% of Bases with Data
ACC	9	16	56
AETC	6	13	46
AFMC	6	10	60
AFSOC	2	3	67
AFSPC	6	8	75
AMC	9	12	75
USAF Academy	0	1	0
TOTAL	38	63	60

ammunition. While over two thirds of installations are now utilizing some form of the lead-free bullet, roughly 29% are still using lead bullets during M16 firing operations. The outdoor to indoor ratio of ranges in operation across the Air Force is roughly eight to one. While the bulk of bases are predominantly conducting firing operations at outdoor ranges, 11% are now shooting within enclosed facilities. Roughly 62% of the ranges located outside have some form of cover and or side walls designed to protect the shooters and instructors from inclement weather as well as shooters, instructors and innocent bystanders from ricocheting bullets; these are designated as semi-enclosed. Due to lack of documentation at various bases, 26% of the range information on bullet traps was found to be unknown. The distribution of those identified, however, show a one to one ratio of hard to soft bullet traps. A complete breakdown of specific range information for each base can be referenced in Appendix B-3.

Table 4.2 Installation Range Information

MAJCOM	Lead	Lead-Free	Unknown	Indoor	Outdoor		Unknown	Bullet Traps		Unknown
					Semi-Enclosed	Open		Hard	Soft	
ACC	5	4	2	1	5	3	0	4	3	2
AETC	2	3	1	0	5	1	0	3	1	2
AFMC	1	5	0	2	2	2	0	4	1	1
AFSOC	1	1	0	0	0	2	0	0	2	0
AFSPC	1	4	1	1	2	3	0	0	5	1
AMC	1	8	0	0	7	2	0	3	2	4
USAF Academy	0	0	0	0	0	0	1	0	0	0
TOTAL	11	25	4	4	21	13	1	14	14	10
% of Bases	29	66	11	11	55	34	3	37	37	26
Percentage totals exceed 100% because several bases use both lead and lead-free bullets										

4.2 Analysis Approach and Relevant Formulas

Once lead sampling results and corresponding range information were compiled, they were next sorted by type of range (indoor or outdoor), type of weapon being fired during sampling, date of sampling, as well as task and workshift TWA exposures. Task exposure is assumed to be representative of the airborne exposure accumulated by an instructor during the duration of actual firing for the M16 Air Force qualification training. Typical firing operations range from one to two hours in length. Unlike the task exposure, the workshift eight-hour TWA exposure is averaged over an eight hour duration and is then comparable to the Air Force Occupational Exposure Limit, or the OSHA compliance standard permissible exposure limit. TWAs are calculated by summing task exposures and averaging them over the duration of an individual's workshift. For compliance, TWAs are calculated over an eight-hour period. The basic

equation used to perform the workshift TWA exposure calculations (Plog, 1996) is shown in Equation 4-1:

$$TWA = \frac{C_1 * t_1 + C_2 * t_2 + C_n * t_n}{480} \quad (4-1)$$

where

C : Concentration (mg/m³) of measurement;
t : time of activity (minutes);
480 = time in an 8-hour workshift (minutes)

All air sampling results collected after the Air Force Engineering Technical Letter 02-11 dated 22 Nov 2002 were excluded from analysis to ensure lead-free ammunition would not affect the average mean lead exposures representative of firing operations during use of leaded ammunition. Lead exposure data for indoor and outdoor ranges were then subdivided into significant population categories for analysis. Workshift TWAs for each category were then plotted as histograms using statistical software (JMP5.1) to determine their natural distribution. Figure 4.1 illustrates the log normal distribution using the lead exposure data from the indoor “M16 only” population category. All other sub-categories of exposure, including “M16 & Unknown” for indoor firing ranges and “M16 Only”, “M16 & M9”, “M16 & M9 & M4”, “M16 and Unknown”, “M16 & M9 & Unknown”, and “M16 & M9 & M4 & Unknown” for outdoor ranges mirrored the lognormal distribution shown.

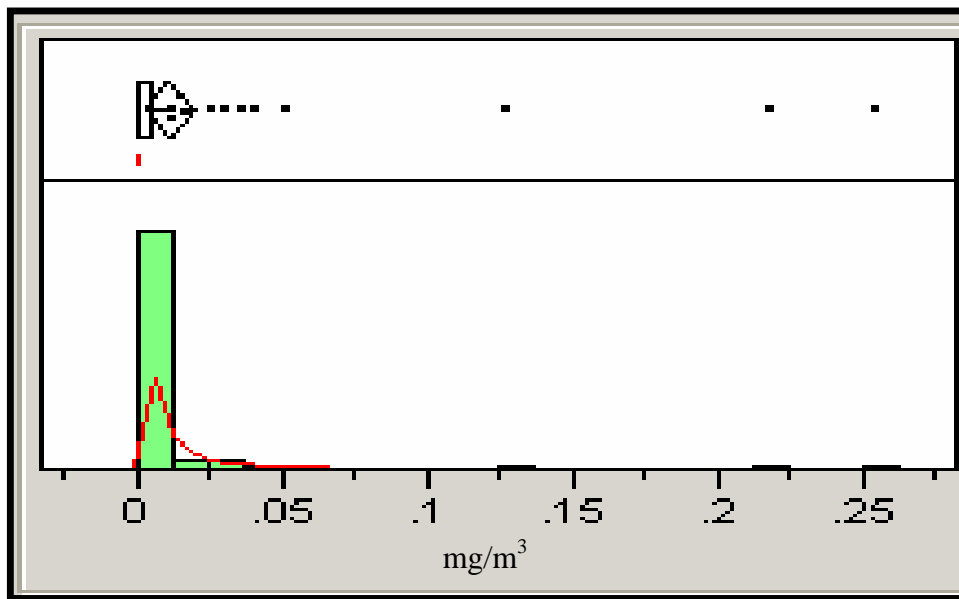


Figure 4.1 Log Normal Distribution of Outdoor M16 Lead Exposure (JMP5.1, 2005)

The arithmetic mean and standard deviation were then calculated for each subcategory of exposure mentioned previously for both indoor and outdoor ranges. The mean tells us the central tendency of the quantitative data being analyzed and can be calculated by simply summing all sample exposures collected for each category and dividing them by the number of samples contained in the data set (McClave, 2005). Once the mean was determined, the standard deviation was calculated to determine the variability in the data. The larger the standard deviation, the more variable the data. The standard deviation was calculated by taking the square root of the sum of the squares of deviation from the mean value divided by one minus the number of samples being analyzed (McClave, 2005). Mean lead exposures, symbolized by \bar{x} , and standard deviation, symbolized by “s” were calculated using equations 4-2 and 4-3 as follows (McClave, 2005):

Arithmetic Mean

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (4-2)$$

where

n = total number of samples
x_i = lead exposure from sample i

Standard Deviation

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (4-3)$$

where

n = total number of samples
x_i = lead exposure from sample i
 \bar{x} = mean lead exposure

Assuming the samples being analyzed were randomly selected from the target population and the lead air sampling data collected from the CONUS bases had a relative frequency distribution that was approximately normal, the 95% confidence interval could be calculated about the mean. The first condition is met due to the entire population being sampled. Since there is currently no straight forward method used to determine confidence limits about the mean for data with a log normal distribution, a naive approach was taken to determine confidence limits for each category of lead exposure data. The first step of this approach was to normalize all the data by taking the natural

log of each exposure. Figure 4.2 shows the same data plotted in Figure 4.1 after being normalized.

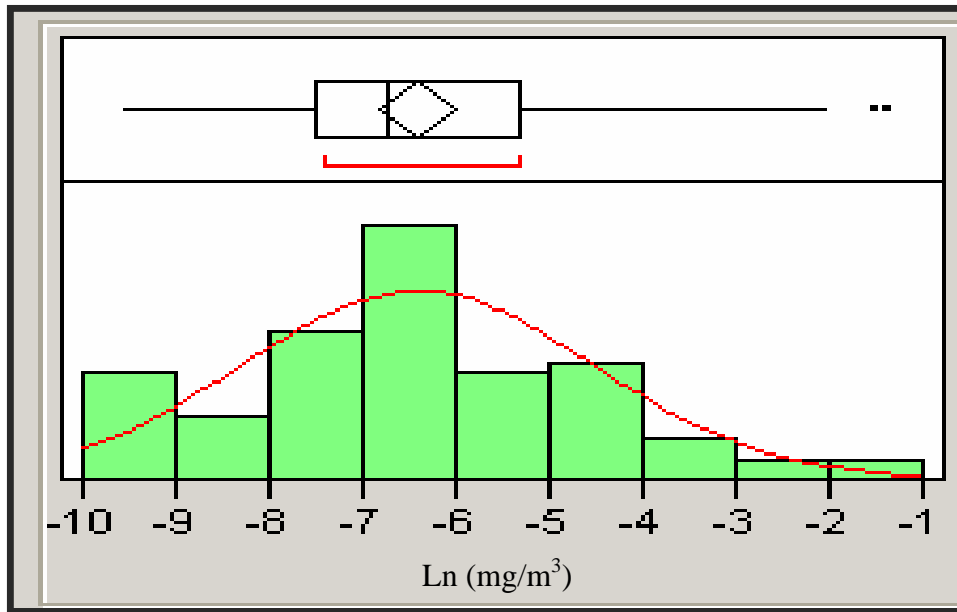


Figure 4.2 Normalized Distribution of Outdoor M16 Lead Exposure (JMP5.1, 2005)

Once the conditions required for a valid small-sample confidence interval had been satisfied, the 95% confidence limits of the normalized data were then calculated for each category using equation 4.4 shown below (McClave, 2005):

Small Sample Confidence Interval for Mean Lead Exposures

$$\bar{x} \pm t_{\alpha/2} \left(\frac{s}{\sqrt{n}} \right) \quad (4-4)$$

where

$\alpha = 0.05$

s = Standard deviation of transformed data

n = total number of samples

\bar{x} = mean lead exposure of transformed data
and $t_{\alpha/2}$ is based on (n-1)degrees of freedom

Critical values of t were extracted from McClave, 2005. A summary table of t-values used to calculate the 95% confidence limits for all analyzed data can be found in Appendix G. Linear interpolation was used to calculate all values not found within the table. For degrees of freedom greater than 120, $t_{0.025}$ was assumed to equal 1.960.

Once confidence intervals had been established for the normalized data for each category, values were then converted back to their original units by taking the natural base (e) of the confidence limit values. Upon completion of this back transformation, a 95% confidence limit about the median was established.

4.3 Lead Exposure Results

Lead exposure data for indoor ranges utilizing leaded ammunition were subdivided into three significant population categories. Each subcategory was developed based on a lack of standardization in exposure grouping at base level during data entry in the CCS. Subcategories were established for indoor ranges based on the potential weapons being fired during sampling and include “M16 Only” air sampling results, “M16 & Unknown” air sampling results, and air sampling results collected during “Back Stop Cleaning and Abatement” activities. “M16 Only” and M16 & Unknown” subcategories were developed to clearly identify the relative lead exposure being generated during M16 firing. Due to a lack of specific information found in the CCS, the central tendency was determined for each subcategory to ensure exposure during M16 firing would not be influenced by results generated by other weapons lumped under this activity. Categories ranged from exposure from “M16 Only” to “M16 and Unknown”

lead exposures not defined within the CCS. In addition, two samples collected during cleaning and abatement operations were also included in a separate category to illustrate a potential additive exposure which may be incurred by some instructors performing these activities as additional duties. Table 4.3 shows a summary of the mean and median workshift 8-hour TWA exposures at indoor shooting ranges during firing of leaded ammunition. Based on the log normal distribution illustrated in Figure 4.1, the median represents a more accurate central tendency of the data than the mean and will be used to represent the average exposure of a given population category. The median will also be used during comparative analysis to lead exposures associated with lead-free bullets. In addition to addressing the central tendency, Table 4.3 also compares representative lead exposure to the lead 8-hour TWA-OEL, 0.05 mg/m^3 .

Table 4.3 shows the results for indoor ranges and indicates the presence of lead exposure during firing operations using conventional lead bullets. Both “M16” and “M16 and Unknown” category numerical descriptive measures were calculated twice due to two unique sampling points significantly higher than all others collected from the CCS warehouse database. Results illustrated in Table 4.3 show “M16 only” and “M16 & Unknown” values calculated including and excluding two elevated samples from Luke AFB. The two samples from Luke AFB indicate 8-hour TWA exposures of 0.675 mg/m^3 and 1.34 mg/m^3 respectively. These values would imply that individuals at this indoor facility were overexposed from 1350 times the OEL to 2680 times the OEL over an eight-hour period. Based on past indoor range studies during conventional leaded ammunition firing discussed in the literature review (Chapter 2), these lead exposure values are exceptionally high and are more likely data entry errors involving units. The

categories where these two high samples were excluded are more likely representative of instructor eight-hour exposures at indoor ranges.

“M16 only” data shows a median eight-hour TWA for lead of 0.006 mg/m^3 and a mean eight-hour TWA of 0.016 mg/m^3 . As shown in Table 4.3, the eight-hour TWA lead concentrations for this category ranged from 0.0003 mg/m^3 to 0.258 mg/m^3 . Results from the “M16 and Unknown” population on the other hand shows a lower median eight-hour TWA value of 0.002 mg/m^3 with lead concentrations ranging from 0.00001 to 0.258 mg/m^3 . Using the upper confidence limit associated with the median as a conservative estimate, exposures from “M16 Only” and “M16 & Unknown” categories range from 6% to 17% of the lead OEL. Although the number of samples supporting the cleaning and abatement median exposure values is limited, there is a strong indication that these activities generate significantly higher lead exposure relative to instructor duties alone. Samples used to calculate representative cleaning and abatement exposure are limited to air sampling results from Fairchild AFB and Seymour Johnson AFB.

Outdoor firing range eight-hour TWA personnel lead exposures are summarized in Table 4.4. Much like exposures found in Table 4.3, lead exposures specific to outdoor firing ranges were also segregated into subcategories. Each subcategory was developed based on a lack of standardization in exposure grouping at base level during data entry into CCS. Subcategories were established for outdoor ranges based on the potential weapons being fired during sampling and include “M16 Only”, “M16 & M9”, “M16 & M9 & M4”, “M16 & Unknown”, “M16 & M9 & Unknown”, and “M16 & M9 & M4 & Unknown”.

Table 4.3 Summary of Workshift Lead Exposures at Indoor Ranges Firing Lead Ammunition

Sample Population	Number of Samples	Mean 8-Hr TWA (mg/m ³)	Median 8-Hr TWA (mg/m ³)	8-Hr TWA Data Range (mg/m ³)	Standard Deviation	95% CL about Median		OEL (mg/m3)	b % of OEL
						LCL (mg/m ³)	UCL (mg/m ³)		
M16 Only	39	0.067	0.007	0.0003- 1.34	5.87E+00	0.004	0.013	0.05	25
M16 Only ¹	37	0.016	0.006	0.0003 – 0.258	3.97E+00	0.003	0.009	0.05	17
M16 & Unknown	91	0.031	0.002	0.00001 – 1.34	8.03E+00	0.002	0.004	0.05	7
M16 & Unknown ¹	89	0.009	0.002	0.00001 – 0.258	6.67E+00	0.001	0.003	0.05	6
Backstop Cleaning & Abatement	4	0.071	0.062	0.036 – 0.121	1.82E+00	0.024	0.162	0.05	324

¹ Two Samples Excluded from Luke AFB because of Data Entry Errors
^b % of OEL Based on Upper Confidence Limit

Table 4.4 Summary of Workshift Lead Exposures at Outdoor Ranges Firing Lead Ammunition

[illegible]

For each subcategory, the mean and median eight-hour TWA exposures were determined to find the central tendency of the data being analyzed. As shown in Table 4.4, the eight-hour TWA lead concentrations for all subcategories ranged from $7.25\text{E-}9 \text{ mg/m}^3$ to 1.14 mg/m^3 . Excluding data concentrations associated with the firing of unknown weapons, the range of eight-hour TWA concentrations is reduced to $7.29\text{E-}5 \text{ mg/m}^3$ to 0.255 mg/m^3 . By comparing the upper confidence limit about the median with the lead OEL, the representative Air Force lead exposure for instructors at outdoor ranges is well below the OEL. In all instances, lead concentrations were found to be five percent or less of the OEL based on the Upper Confidence Limit about the median. While the central tendency in both Table 4.3 and Table 4.4 are both well below the lead OEL of 0.05 mg/m^3 , there are bases with substantial lead exposures (as shown in the range values) that did in fact exceed the limit designed to protect instructors from adverse health effects.

In order to determine if the use of lead-free bullets significantly reduces lead exposure generated during firing operations, lead samples were collected at both inside and outside ranges during M16 Air Force Qualification Training during this study. By comparing the difference in lead exposure at each individual base (lead ammo data from data call; lead-free collected during study), the number of confounding factors can be substantially reduced and thus increase the confidence in our descriptive analysis. Based on results presented in Table 4.5, lead exposure to instructors at indoor ranges at Hill and Wright Patterson AFB has been reduced by roughly 70% by use of lead-free ammunition. Lead exposure at the outdoor open range at McGuire AFB on the other hand only showed a 41% reduction in lead exposure. Differences in lead reduction at indoor and outdoor

ranges could be directly attributed to variable wind directions and speeds at outdoor ranges.

Table 4.5 Lead Exposure Comparison between Lead and Lead-Free Ammunition

Installation	Type of Bullet	Number of Samples	8-Hr TWA (mg/m ³)		Standard Deviation	% of OEL	% Reduction in Lead Exposure
			Median	Mean			
Hill	Lead	20	0.0061	0.0143	2.41E-02	12	70
Hill	Lead-free	9	0.0018	0.0016	4.53E-04	4	
McGuire	Lead	9	0.0017	0.0013	5.27E-04	3	41
McGuire	Lead-free	9	0.0010	0.0010	1.84E-04	2	
Wright Patterson	Lead	58	0.0024	0.0448	1.60E-01	5	73
Wright Patterson	Lead-free	9	0.0006	0.0006	1.84E-04	1	
% Reduction in Lead Exposure Based on Median							

As expected, exposure data from lead-free bullets also show a parallel reduction in the central tendency of the lead, relative to the lead OEL. Although the comparison presented in Table 4.5 suggests a significant lead exposure reduction attributed to the change in ammunition, it is important to note that representative lead exposures generated during both lead and lead-free firing are well below the lead OEL. Figure 4.3 illustrates both the reduction in lead as well as the lead OEL.

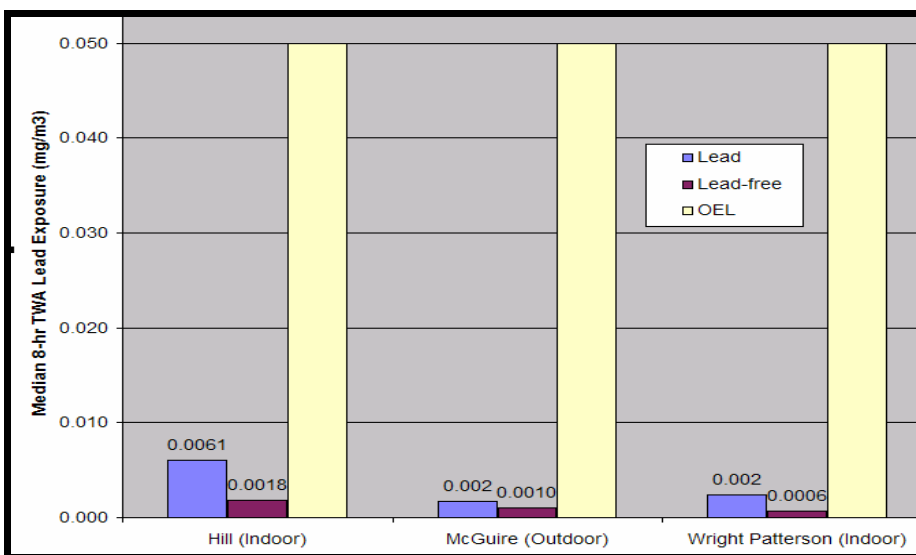


Figure 4.3 Reduction in Lead Exposure due to Transition to Lead-Free Bullets

4.4 Lead-Free Ammunition Exposure Results

Personal air sampling results collected during this study indicate that all chemical compounds sampled at the outdoor firing ranges at Ellsworth AFB, Whiteman AFB, McGuire AFB, and Offutt AFB were well below the occupational exposure limits. Low concentrations of copper and trace levels of zinc were detected at all four outdoor ranges. Looking at all facilities, the eight-hour TWA concentrations for copper ranged from 0.0377 mg/m³ to 0.2040 mg/m³. The eight-hour TWA concentration for zinc ranged from 0.0019 mg/m³ to 0.0250 mg/m³. In addition to small concentrations of zinc and copper, aluminum was also sampled and detected at Whiteman AFB, McGuire AFB, and Offutt AFB. At those bases, concentrations of aluminum were found to range from 0.002 mg/m³ to 0.011 mg/m³. Both aluminum and zinc compounds were found to be less than 1% of their respective OELs while copper compounds were found to be roughly 1.3% of the OEL. All other sampled metals were found to be below their respective detection

limits. All nylon and plastic byproducts associated with lead-free ammunition were also found to be below their respective detection limits with the exception of phosgene.

Traces of phosgene were detected at Ellsworth AFB. Table 4.6 summarizes the mean and median task and eight-hour TWA workshift exposure data and the standard deviation and confidence limits about the median for four outdoor firing ranges during M16 firing of lead-free ammunition. Data was combined for the four bases. It is important to note the size of the confidence intervals are extremely large due to the limited number of samples taken. Because of the small sample number, the 95% confidence interval presents little to no value for discussion regarding realistic instructor exposures. Base specific results for these outdoor ranges are summarized in Appendix H-1. Personal air sampling results indicate that all compounds sampled at the indoor firing ranges at Hill AFB and Wright Patterson AFB during use of lead-free ammunition were

Table 4.6 Summary of Exposure at Four Outdoor Ranges Firing Lead-Free Ammunition

Analyte	Number of Samples	Task Exposure (mg/m ³)		8-Hr TWA (mg/m ³)		Standard Deviation	8-Hr TWA Data Range (mg/m ³)	95% CL (about Median)		TWA Standard (mg/m ³)	% OEL	
		Mean	Median	Mean	Median			LCL (mg/m ³)	UCL (mg/m ³)			
Aluminum	19	0.019	0.0153	0.0033	0.0029	4.12E+02	0.0019 - 0.0110	0.0002	0.0521	10	<	0.03
Barium	9	0.266	0.0706	0.0004	0.0004	1.00E+00	0.0004 - 0.0005	0.0004	0.0004	10		0
Copper	21	0.807	0.5240	0.0468	0.0132	8.85E+01	0.0377- 0.2040	0.0017	0.1016	1		1.3
Zinc	21	0.163	0.1524	0.0067	0.0042	2.76E+02	0.0019 - 0.0250	0.0003	0.054	10		0.04
HCL	12	1.252	1.1983	0.1473	0.0952	1.37E+01	0.0560 - 0.8450	0.018	0.503	-	<	-
HCN	21	0.434	0.3570	0.0271	0.0268	4.20E+01	0.0140 - 0.0380	0.0049	0.1467	11.1	<	0.2
NH ³	17	0.236	0.1988	0.1976	0.1964	6.56E+00	0.1583 - 0.2170	0.0746	0.5167	17.4	<	1.1
NO	9	0.030	0.0267	0.0846	0.0637	2.03E+01	0.0220 - 0.1800	0.0063	0.6446	30.7	<	0.2
NO ₂	11	0.039	0.0225	0.0445	0.0371	3.31E+01	0.0100 - 0.0800	0.0035	0.39	5.6	<	0.7
Phosgene	11	0.002	0.0022	0.0043	0.0042	3.11E+02	0.0040 - 0.0072	0.0001	0.1994	0.4		1.1

well below the occupational exposure limits. Even when examined on a task basis, all compounds had very low concentrations in air. Low concentrations of copper and trace levels of zinc were detected at both indoor facilities. All other analytes were found to be below their respective detection limits. The eight-hour TWA concentrations for copper ranged from 0.0015 mg/m³ to 0.0350 mg/m³; for zinc from 0.001 mg/m³ to 0.0107 mg/m³. All metals and compounds were found to be less than 3% of their respective OELs. Table 4.7 summarizes the mean and median workshift exposure for two indoor firing ranges during M16 firing of lead-free ammunition. Due to the low number of samples taken, 95% confidence intervals for this data are large and add very little value for discussion. As a result, confidence limits were not reported as seen previously. Base specific results for Hill AFB and Wright Patterson AFB are summarized in Appendix H-2.

Table 4.7 Summary of Exposure at Hill AFB & Wright Patterson AFB Indoor Ranges Firing Lead-Free Ammunition

Analyte	Number of Samples	Mean Task (mg/m ³)	Median Task (mg/m ³)	Mean 8-Hr TWA (mg/m ³)	Median 8-Hr TWA (mg/m ³)	8-Hr TWA Data Range (mg/m ³)	TWA Standard (mg/m ³)	% OEL
Barium	13	0.0052	0.0062	0.0011	0.0009	0.0004 – 0.0021	10	0.01
Copper	18	0.0087	0.0081	0.0086	0.0050	0.0015 – 0.0350	1	0.50
Lead	13	0.0061	0.0062	0.0013	0.0011	0.0005- 0.0021	0.05	2.27
Tin	6	0.0070 ^b	0.0069 ^b	0.0018	0.0018	0.0015 – 0.0021	2	0.09
Zinc	13	0.0109	0.0081	0.0028	0.0023	0.001 – 0.0107	10	0.02
NH3	9	0.88 ^b	0.81 ^b	0.2179	0.2125	0.1778 – 0.3469	17.4	1.22
HCN	9	0.15 ^b	0.16 ^b	0.0380	0.0380	0.0360 – 0.0400	11.1	0.34
% OEL Based on Median								
^b Task Exposure Based on Samples from Hill AFB Only								

In addition to collecting metals and byproduct samples associated with plastics and nylon, direct reading instruments were also used to screen for combustion byproducts at Hill AFB and Offutt AFB firing ranges during M16 firing of lead-free ammunition. The chemicals screened included carbon monoxide, nitric oxide, and nitrogen dioxide. Screening for nitric oxide and nitrogen dioxide were not conducted at Hill AFB due to a lack of available equipment. Table 4.8 summarizes minimum, maximum and average concentration levels present during firing operations. Analyte concentrations averaged over the full duration of the shooting period were found to be well below their respective OELs. Maximum concentrations were generated immediately after weapons had been discharged and were dissipated within seconds.

Table 4.8 Combustion Concentrations Present During Firing Lead-Free Ammunition

Installation	Analyte	Sample Date	Sample Time (min)	Min (ppm)	Max (ppm)	Avg (ppm)	OEL (ppm)
Hill	CO	21 Sep 05	130	0	54	0	25
Hill	CO	23 Sep 05	89	0	204	2	25
Offutt	CO	7 Nov 05	90	0	62	8	25
Offutt	CO	9 Nov 05	118	0	103	5	25
Offutt	NO	7 Nov 05	90	0	1	0.2	25
Offutt	NO	9 Nov 05	118	0	0.8	0.2	25
Offutt	NO ₂	7 Nov 05	90	0	0	0	3
Offutt	NO ₂	9 Nov 05	118	0	0	0	3

4.5 Base Specific Observations

Specific observations and relevant discussion for lead-free firing operations at Hill AFB and McGuire AFB are discussed below. Findings for Ellsworth AFB, Whiteman AFB, and Offutt AFB can be found in Appendix D-3, D-4, and D-5.

4.5.1 McGuire AFB

Four of the nine ammonia samples collected for the outdoor range at McGuire AFB were not considered in this analysis due to pump failures during sampling. Although all sample results were reported below the detection limit, insufficient volumes were collected to provide representative samples for the full duration of M16 firing operations. On each day of sampling, one instructor was observed taking a five minute smoke break during the duration of the sampling period. Based on sample results collected on the 2nd and 3rd of November, smoking has no apparent affect on exposure concentrations during firing operations involving lead-free ammunition. Average wind speeds ranged from a minimum of 300 fpm (3 knots) to 1100 fpm (11 knots) for the three days of air sampling at McGuire AFB. On the 2nd of November, wind was recorded to be flowing 1100 fpm on average in the south easterly direction directly into the breathing zone of instructors and shooters, as measured using a TSI ALNOR CompuFlow (TSI, Minnesota) Model No. 8585 velometer. Slightly elevated results of copper concentrations collected on the 2nd of November, relative to the 3rd and 15th, where winds were predominantly blowing down range away from the instructors and shooters, suggest that wind speed and direction have a direct influence on exposure levels during firing operations.

4.5.2 Hill AFB

Low concentration levels of all chemicals at the indoor firing range at Hill AFB can be attributed to a number of in place engineering and administrative controls. In addition to using lead-free ammunition during M16 qualification training, this indoor facility is also equipped with an automatic target retrieval system and a perforated floor

to ceiling supply wall designed to provide uniform air distribution across the firing line.

Past smoke tests performed by the Hill AFB Bioenvironmental Engineering Flight indicated laminar flow throughout the range with only minor eddy currents being produced. Eleven air flow velocities were collected at the firing line at even intervals between firing stations 1 and 21 using an ALNOR CompuFlow 8570 velometer and compared with the minimum 50 ft/min velocity and recommended design velocity of 75 ft/min outlined in the Indoor Firing Ranges Industrial Hygiene Technical Guide (Department of the Navy, Dec 99; Department of the Air Force, Nov 05). Figure 4.4 shows a plan view of the range configuration with air flow velocities collected at the firing line for the purpose of this study. Velocities recorded at the firing line ranged from 55 ft/min to 160 ft/min with an average velocity of 82 ft/min.

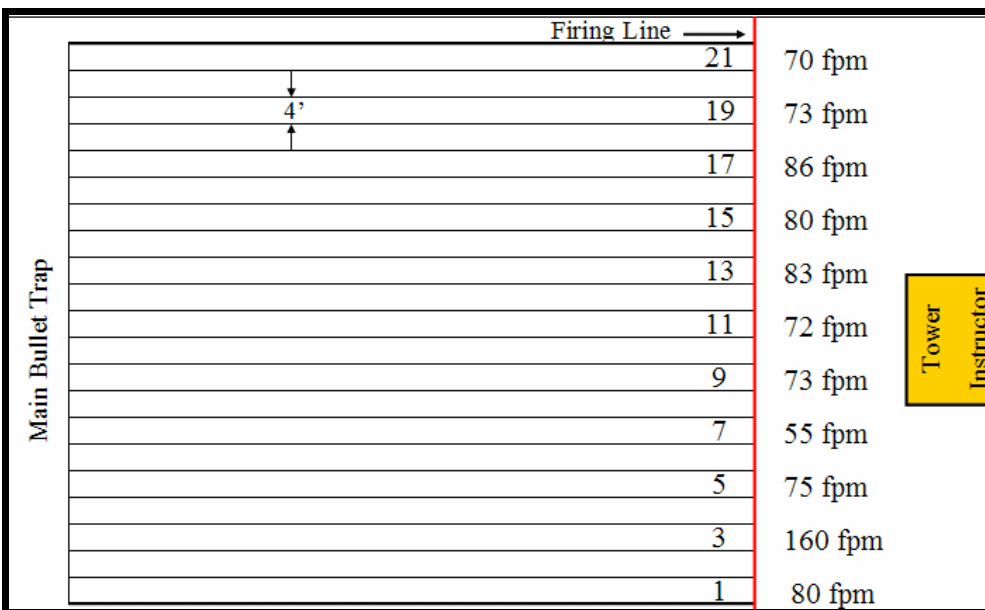


Figure 4.4 Hill AFB Plan View of Air Flow Velocities at Firing Line

In addition to engineering controls, a contract has been in place since March 2004 to remove spent projectiles and other hazardous debris from the firing range on a quarterly basis. By contracting out this task to non-Air Force employees, instructors are able to eliminate the additional elevated exposures generated during cleaning operations which likely put them in jeopardy of exceeding specific OELs designed to prevent the onset of adverse health effects.

4.6 General Discussion & Conclusions

Lead air sampling results from using leaded ammunition indicate that the central tendency of eight-hour TWA lead concentrations range from 3% to 17% of the Air Force OEL. At first glance, it may appear that there should be no major concerns since the median lead exposures presented are below the OEL as well as the action limit of 0.025 mg/m³. It is however important to note that there are still installations firing leaded ammunition that are well above the Air Force OEL and are thus prone to lead exposures capable of causing adverse health effects. Furthermore, if we were to consider the worst case scenario by assuming firing operations were to increase to a maximum duration of eight hours a day, five times a week, instructors could potentially be exposed to lead concentrations up to 0.0582 mg/m³ (1.2 times the OEL). The worst case scenario was determined using the 95% upper confidence limit of the “M16 only” median task exposure shown in Table 4.14 of Appendix H-3. With this nation at war and the constant closure of military installations, the assumption used to estimate worst case lead exposures would be considered reasonable.

Comparison of median lead exposures seen in Table 4.5 generated from firing leaded ammunition at indoor and outdoor ranges suggests that personal lead exposures

within indoor ranges are greater than those at outdoor firing ranges. This difference in breathing zone exposures is most likely attributed to lack of routine cleaning at indoor ranges combined with bad administrative practices and inadequate ventilation systems. While natural ventilation provided at outdoor ranges can be quite variable, winds blowing predominantly down range have the ability to carry lead contaminants away from the instructor's breathing zone and thus reduce the overall lead exposure accumulated over the task duration.

With roughly two thirds of installation ranges currently using frangible lead-free ammunition, it is more than appropriate to discuss some of the exposures and findings identified during lead-free operations at both indoor and outdoor ranges. As expected, lead concentrations were significantly reduced by the transition from lead to lead-free bullets. Assuming all facility conditions remained relatively constant during the use of lead and lead-free ammunition, the reduction of lead exposure found at the two indoor firing facilities is likely attributed to the transition to the frangible lead-free bullets. Based on results of this study, it is not unreasonable to conclude that the lead-free ammunition manufactured by Olin Winchester and the Federal Cartridge Company presents no known adverse health hazards associated with lead.

Other metals found in lead-free ammunition as well as the combustion by-products associated with nylon and plastics used to bind them together were also studied to ensure constituents were not presenting a new potential exposure hazard of equal or greater toxicity. This study was focused on instructor exposure and was thus limited to only areas in which instructors traversed during the period of the M16 shooting activity. Of the analytes sampled, only small traces of zinc, copper, aluminum and phosgene were

detected above their level of detection. Personal air sampling exposure showed all metals as well as plastic and nylon by-products to be well below their applicable OELs. Using the task TWA exposure found in Table 4.7 and Table 4.8 to assume worst case conditions as discussed for leaded ammunition, all breathing zone samples were still found to be below their applicable OELs.

Based on the central tendency results, this research suggests that the exposure levels associated with lead and lead-free ammunition does not pose a significant threat to the majority of Air Force instructors at indoor and outdoor ranges. If operation tempo increases for Air Force ranges using lead and lead-free ammunition to the extent that instructors are exposed to the equivalent of the task exposure however, occupational exposure limits may be exceeded at firing ranges using leaded ammunition.

V. Conclusions

5.1 Overview

This chapter readdresses the potential adverse health concerns generated in response to transitioning from lead to frangible lead-free ammunition during M16 firing operations at indoor and outdoor shooting ranges. Research questions presented in Chapter I will be answered based on information collected from the historical data request as well as the quantitative and qualitative results obtained during firing of lead-free ammunition at six active duty Air Force CONUS installations. The main focus questions and corollary questions to be answered are reiterated below.

(1) How many bases have transitioned to lead-free ammunition? What is the maximum and average lead exposure during small arms qualification training using both lead and lead-free bullets? How much is lead exposure reduced through the use of lead-free bullets?

(2) What other potential airborne chemical exposures have been introduced to Air Force instructors and shooters during small arms weapon qualification training as a result of the transition to Green Bullets?

In addition to summarizing overall results, this chapter will also build conclusions, cite limitations, and discuss recommendations gleaned from this research. Finally, future research will be suggested to better understand other areas of concern related to lead-free ammunition currently being implemented across the majority of the Air Force firing.

5.2 Results

Firing range information collected from the data request sent to 63 CONUS installations as well as that collected from the CCS database warehouse suggests roughly 66% of firing ranges are currently firing lead-free bullets compared to leaded ammunition during M16 qualification training. Based on range configuration information compiled from 38 of the 63 bases polled, only 11% of ranges across the Air Force are currently performing firing operations within indoor facilities. Of the remaining 89%, 21 installations are conducting firing operations at semi-enclosed ranges while 13 perform this activity at shooting ranges completely open to the environment. The type of bullet traps being used across the Air Force during firing operations was inconclusive due to a significant lack of detailed responses reported from each installation. Range information received did, however, suggest a 50/50 ratio of ranges using hard traps as opposed to soft traps to collect spent ammunition.

Maximum and average lead exposures reported during firing of leaded ammunition were based on air sampling results performed by previous Bioenvironmental Engineering Flights dating back to 1986. Results indicate eight-hour TWA lead exposures directly associated with M16 firing operations at indoor facilities range between 0.0003 mg/m^3 and 0.258 mg/m^3 with a median eight-hour TWA of 0.006 mg/m^3 . In the event that instructors were to perform this task over the course of an entire eight-hour workshift, personnel could potentially be exposed to lead concentrations of 0.0582 mg/m^3 . This potential lead exposure represented by the task exposure is approximately 1.2 times the Air Force OEL of 0.05 mg/m^3 . M16 firing of leaded ammunition at outdoor

firing ranges showed a similar range of lead concentrations to those found at indoor facilities with a slightly lower median eight-hour TWA exposure of approximately 0.001 mg/m³. In addition to potential exposures generated during M16 firing, limited air sampling results collected during range cleaning and abatement operations suggest that individuals performing these activities would more than likely accumulate additional lead exposure significantly higher than those instructors performing only duties specific to firing operations, with eight hour exposures ranging from 0.036 to 0.121 mg/m³ as an eight-hour TWA.

The amount of lead reduction attributed to the transition from lead to lead-free bullets was calculated by comparing lead exposures generated during the use of leaded bullets with those generated during the use of lead-free ammunition at three separate installations; all other parameters were assumed to remain relatively constant. Results showed approximately a 70% reduction in airborne lead concentrations at indoor ranges and a 41% reduction in airborne lead concentrations for outdoor ranges. However, there are many factors that may have contributed to the lead exposure reductions illustrated by this research. Other contributing factors might include changes in administrative procedures, wind speed and wind direction at outdoor ranges, and upgrades to existing range configuration at indoor ranges. Upgrades to indoor range configuration may include more efficient ventilation systems, automatic target retrieval systems, and/or variations of bullet trap collection systems.

In addition to analyzing lead exposures generated during M16 firing of leaded ammunition, comprehensive evaluations were also conducted at installations firing lead-free ammunition to ensure that the lead hazards associated with leaded bullets were not

simply being substituted with another form of ammunition capable of generating other exposures of equal or greater toxicity. Analytes of interest sampled during the firing of green bullets included aluminum, barium, copper, lead, tin, zinc, ammonia, hydrogen cyanide, nitric oxide, nitrogen dioxide, and phosgene. Personal air sampling results representative of instructor exposure showed that all metal concentrations, as well as plastic and nylon by-products, were well below their applicable OELs and in most instances less than the limit of detection. Even when assuming worst case exposures represented by task exposures for each analyte sampled, breathing zone samples were still found to be well below their applicable OELs.

5.3 Limitations and Assumptions

There are several assumptions and limitations associated with this study. The exact implementation date for installation transition to the frangible lead-free ammunition was not well established. A 2002 Engineering Technical Letter approved use of lead-free ammunition as an alternative to leaded ammunition but did not mandate that all bases comply. Although a clear transition date was not established by this letter, the date of the letter was assumed as the implementation start date for transition to lead-free ammunition to ensure any lead-free air sampling results would not influence analysis for leaded ammunition.

Sample results extracted from the CCS (that have been input by numerous individuals) are subject to many variables that could affect their reliability. Due to the low level of detail captured within this database, data is subject to several limiting factors. Limiting factors include failure to consider the possibilities of consecutive samples, unclear identification of sample locations leading to misrepresentation of true

breathing zone exposures, as well as data entry errors made by personnel upon receipt of sample results. By not considering consecutive samples, task exposures as well as eight-hour TWA exposures may be considerably underestimated. Failure to identify sample location and type of sample (personal or area) could also skew the true central tendency of the data being analyzed. This research assumed each sample collected was representative of the entire firing duration of the activity and that all samples were representative of realistic instructor exposures. Potential gross data entry errors due to incorrect units, as evident by two unrealistic air sampling results entered by Luke AFB suggesting instructor exposures to be over 1350 times the OEL, were identified during analysis and were removed to prevent skewing the data.

Due to accuracy of equipment and variation in sampling technique caused by personnel change over at each installation, sampling results may vary over time. In addition to the variability attributable to the potential for different sampling strategies, upgrades in facilities to include more efficient ventilation systems, bullet traps and other engineering controls designed to reduce personal exposure may also affect data being analyzed. Facilities and engineering controls designed to reduce the potential for exposures were assumed to be constant unless clearly identified in firing range information collected from each installation.

Overarching conclusions made regarding sampling results collected during lead-free ammunition also assume comparable engineering controls are in place at all firing ranges and that only frangible lead-free ammunition manufactured by Olin Winchester and the Federal Cartridge Company are being fired. Other potential ammunition

introduced at indoor and outdoor firing ranges designed for the purposes of a suitable substitute for conventional lead bullets would require further analysis.

5.4 Research Recommendations

Findings from this research suggest that a significant reduction in lead exposure can be accomplished by transitioning to Frangible Non-toxic Ammunition, manufactured by Olin Winchester, or Ballisticlean ammunition, manufactured by the Federal Cartridge Company. In addition to reducing lead exposures, results from air sampling conducted during firing of these frangible lead-free bullets at six Air Force firing ranges also suggests that the exposures associated with the metal constituents and nylon and plastic by-products are well below the OEL. Based on results associated with the two specific types of frangible lead-free ammunition analyzed within this study, this research supports the recommendation to fully implement the use of these specific frangible lead-free bullets at all indoor and outdoor shooting ranges across the Air Force. Further research, however, would be warranted if other frangible lead-free bullets were to be considered for use. Additionally, since it is unclear if lead-free ammunition is the sole engineering control responsible for minimizing potential exposure to Air Force instructors, further research is also recommended at indoor firing ranges to determine the additive affect associated with other engineering controls currently in place. With that being said, ranges firing lead-free ammunition with personnel experiencing eye or nasal irritation should ensure ventilation systems are operating adequately to produce a velocity of 75 feet per minute on the firing line to ensure any potentially stagnant airborne irritants are

blowing down range and away from the instructors breathing zone (Department of the Navy, Dec 99; Department of the Air Force, Nov 05).

In addition to the recommendations primarily designed to address exposures at small arms firing ranges, attention to detail when populating the CCS database is recommended. Since the CCS database warehouse was designed to serve as a repository of information for Bioenvironmental Engineers and other agencies specific to different activities being performed across the Air Force, the input of good quality data is critical. In doing so, we can build confidence in the exposure data being preserved and potentially use that data in the future to address and solve problems like the one presented in this thesis.

5.5 Additional Research

Other environmental and human health concerns associated with lead-free ammunition at indoor and outdoor firing ranges must still be addressed in order to fully understand the implications of replacing conventional leaded ammunition with frangible lead-free ammunition. This section discusses recommendations for additional studies, ranging from quantifying the reduction in exposures due to engineering controls to performing a life cycle cost analysis on the use of lead-free frangible bullets at Air Force shooting ranges.

5.5.1 Evaluation and Quantification of Engineering Controls

This research concluded that Air Force instructors working at ranges firing lead-free ammunition are not in jeopardy of being over exposed to metals or by-products at levels associated with adverse health effects. Since engineering and administrative controls were in place at the time of sampling, it is safe to conclude that instructors are

well below their respective OELs under current range conditions. Since using lead-free ammunition may in fact eliminate all potentially toxic airborne health exposures at the source, additional sampling could be conducted at indoor ranges to determine if, for example, the presence of a ventilation system is truly needed to control occupational exposures associated with lead-free ammunition. In addition to quantifying the actual reduction in exposures due to the ventilation system, additional air sampling could be conducted to determine further reductions in exposure attributed from automatic target retrieval systems as well as other engineering and administrative controls. In the event that a given engineering control is not required to control a specific hazard, removal of this control could prove to be a significant savings in operation and maintenance cost for the Air Force.

5.5.2 Exposures Generated from Cleaning Operations

If lead-free ammunition poses no health hazard during firing operations, the next logical step is to determine if instructors performing range cleaning activities will generate an additional significant exposure capable of exceeding the occupational exposure limits designed to protect the Air Force employee. A similar sampling strategy could be employed to capture representative breathing zone samples of range instructors performing these additional duties. Once samples are collected and analyzed, exposure levels generated can be added to the personal exposure generated during firing operations to determine the total exposure potentially received by Air Force instructors. If the total exposure levels remain well below their respective Air Force OELs, these activities can be performed without the use of additional personal protective equipment (PPE). If PPE is not required to perform these duties, the physical burden on instructors performing this

additional duty may be alleviated or future costs associated with contracting out this service could be reduced significantly.

5.5.3 Environmental Impacts Associated with Lead-Free Ammunition

With over 80% of the Air Force ranges being outside to some degree or another, there is still a concern on the environmental impacts associated with the transition to lead-free ammunition. In order to ensure that the military has not simply substituted leaded ammunition of known toxicity with a comparable bullet potentially comprised of other toxic heavy metals, volatile organic compounds or ozone depleting chemicals, further studies involving several different lead-free bullets should be explored to determine the best environmental alternative. Specific areas of interest should include the fate and transport of these associated chemicals through different media to determine the extent of accumulated environmental damage over time, perhaps through modeling.

5.5.4 Sustainable Design Look at Using Lead-Free Ammunition

Research performed in this study suggests that the transition from lead to lead-free ammunition at two thirds of CONUS Air Force firing ranges has led to a less toxic environment for Air Force instructors. If the transition to lead-free ammunition is also found to reduce the amount of impact on the environment throughout the life cycle of the bullet, there could be a significant reduction associated with clean up-costs for the military. As a result of lead being replaced by safer components in these green bullets, these bullets may be categorized as sustainable products. By performing a life cycle cost analysis for ranges using lead-free bullets as opposed to those currently using conventional leaded ammunition, the Air Force may be able to determine the reduction in the long term cost savings associated with the resource management decision of

transitioning from lead to lead-free bullets. In addition to monetary savings associated with this transition, potential environmental impact savings may also be realized.

5.6 Closing Comments

In conclusion, Air Force instructors at indoor and outdoor ranges firing lead and lead-free ammunition are not exposed to significant airborne lead concentrations known to cause adverse health effects. If operation tempo increases at ranges using lead and lead-free ammunition to the extent that instructors are exposed to the equivalent of the task exposure however, occupational exposure limits may be exceeded at firing ranges using leaded ammunition. Results collected from the four outdoor firing ranges and two indoor facilities within this study strongly suggest that Air Force instructors at firing ranges using frangible lead-free ammunition manufactured by both Olin Winchester and the Federal Cartridge Company (NSN 1305-01-463-8232) are currently not being exposed to significant concentration levels of metals and plastic or nylon combustion by-products known to potentially lead to adverse health effects. Considering all findings and results discussed in this research, the best way to reduce the potential for toxic chemical airborne exposure to Air Force instructors, thus preserving the government assets charged with training our men and women to go into battle, is in fact to “get the lead out” and make a 100% transition to these frangible lead-free bullets.

Appendix A: Internal Dose Associated with Health Effects from Selected Studies (USDHHS, 1999)

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
Cardiovascular						
840 M, 67 yrs old (mean)	General population	6.1 (mean)	20 (mean tibia); 29 (mean patella)	Hypertension	Longitudinal study (Normative Aging Study). Covariates: age and body mass index; race; family history of hypertension; education; tobacco smoking and alcohol consumption; and dietary intakes of sodium and calcium.	Cheng et al. 2001
677 pregnant F, 15–44 yrs old	General population	1.9 (geometric mean)	8 (mean tibia); 11 (mean calcaneus)	Hypertension	Longitudinal study of pregnancy. Co-variables: age and body mass index, parity, postpartum hypertension, tobacco smoking, and education.	Rothenberg et al. 2002b
496 adults, 56 yrs old (mean)	Occupational	4.6 (mean)	14 (mean)	Increase in systolic blood pressure	Longitudinal study. Covariates: age and body mass index; diagnosis of diabetes, arthritis, or thyroid disease; education; and blood pressure measurement interval.	Glenn et al. 2003
294 F, 61 yrs old (mean)	General population	3 (mean) <1–14 (range)	13 (tibia) 17 (patella)	Hypertension	Case-control study (Nurses Health Study). Covariates: age and body mass index, dietary sodium intake, and family history of hypertension.	Korrick et al. 1999
630 M, 67 yrs old (mean)	General population	7 (mean)	24 (mean tibia) 21 (mean patella)	Hypertension	Case-control study. Covariates: body mass index and family history of hypertension.	Hu et al. 1996a
13,871 M and F, >20 yrs old	General population	2.3 (median) 1.4–3.9 (inter-quartile range)	NM	Increase in systolic and diastolic blood pressure	NHANES III analysis. Covariates: age and body mass index; hematocrit, total serum calcium, and protein concentrations; tobacco smoking; alcohol and coffee consumption; dietary calcium, potassium, and sodium intakes; diabetes; and use of antihypertensive drugs.	Den Hond et al. 2002

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
216 F, 48 yrs old (mean)	General population	2.9 (mean) 0.5–31 (range)	NM	Diastolic hypertension	NHANES III analysis. Covariates: race, age, and body mass index; tobacco smoking, and alcohol consumption.	Nash et al. 2003
509 M and F, 19–24 yrs old	General population	<15 (exclusion criterion)	>10	Increase in systolic and diastolic blood pressure	Cohort follow-up study of Bunker Hill children. Covariates: gender, age, and body mass index; blood hemoglobin and serum albumin concentrations; education; tobacco smoking and alcohol consumption; current use of birth control pills; income; and current PbB.	Gerr et al. 2002
775 M, 68 yrs old (mean)	General population	6 (mean)	22±13 (tibia) 31±19 (patella)	EKG changes and conduction defects	Cross-sectional study (Normative Aging Study). Covariates: age, body mass index, diastolic blood pressure, fasting blood glucose level, alcohol consumption, and serum HDL concentration.	Cheng et al. 1998a
<u>Gastrointestinal</u>						
Children	General population	60–100 (range)	NM	Colic	Compilation of unpublished data.	NAS 1972
<u>Hematological</u>						
159 adults	General population and occupational	5–95 (range)	NM	Decreased ALAD activity	Four groups of subjects were analyzed. One unexposed group and three worker groups.	Hernberg and Nikkanen 1970
579 children, 1–5 yrs old	Residence near lead ore smelter	>20	NM	Anemia	Anemia defined as hematocrit <35%. Iron status was not available.	Schwartz et al. 1990
143 children, 10–13 yrs old	Residence near lead smelter	5–40 (range)	NM	Decreased ALAD activity	There was no obvious threshold for ALAD-PbB relationship. A threshold for elevation of EP was evident between 15 and 20 µg/dL PbB.	Roels and Lauwerys 1987

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
Musculoskeletal						
290 children, 6–10 yrs old	General population	2.9 (mean)	NM	Increased caries in urban children	No increase in caries was seen in 253 rural children (PbB, 1.7 µg/dL). Covariates: sex, race, SES, maternal smoking, parental education, and dental hygiene variables.	Gemmel et al. 2002
Renal						
744 M, 64 yrs old (mean)	General population	8 (mean) <4–26 (range)	NM	Decrease in GFR	Cross-sectional study (Normative Aging Study). Covariates: age and body mass index; systolic and diastolic blood pressure; alcohol consumption and tobacco smoking; and analgesic or diuretic medications.	Payton et al. 1994
459 M, 57 yrs old (mean)	General population	10 (mean) 0.2–54 (range)	NM	Decrease in GFR	Longitudinal study (Normative Aging Study). Covariates: age and body mass index; hypertension; alcohol consumption and tobacco smoking; and education.	Kim et al. 1996a
707 M, 62 yrs old (mean)	General population	6.5 (mean)	21 (tibia) 32 (patella)	Decrease in GFR	Prospective study (Normative Aging Study). Covariates: age and body mass index; diabetes and hypertension; alcohol consumption and tobacco smoking; and education.	Tsaih et al. 2004
20,000 M and F, >20 yrs old	General population	3.3 (mean)	NM	Decrease in GFR	NHANES III analysis. Covariates: age, gender, and body mass index; systolic blood pressure; cardiovascular disease and diabetes mellitus; alcohol consumption and cigarette smoking; and household income, marital status, and health insurance.	Munther et al. 2003
1,981 M and F, 48 yrs old (mean)	General population	11 (mean) 2–72 (range)	NM	Decrease in GFR	Cross-sectional study (Cadmbel Study). Covariates: age and body mass index; urinary glutamyltransferase activity; diabetes mellitus; and analgesic or diuretic therapy.	Staessen et al. 1992

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
Endocrinological						
75 men	Occupational	50–98 (range)	NM	Decreased serum T3 and T4	No significant correlation for FT4 and TSH in this PbB range. TSH, T3 and T4 increased in the range 8–50 µg/dL.	López et al. 2000
68 children, 11 mo–7 yrs old	General population	2–77 (range) 25 (mean)	NM	No effect on serum T4 or FT4	Covariates: sex, race, SES, and hemoglobin; 66% of the children had PbB <24 µg/dL.	Siegel et al. 1989
30 children, 1–5 yrs old	General population	33–120 (range)	NM	Decreased serum Vitamin D levels	15 children with mean PbB of 18 µg/dL served as a comparison group.	Rosen et al. 1980
Immunological						
38 children, 3–6 yrs old	General population	>10	NM	Increased IgE and decreased IgG and IgM in F	35 children with PbB <10 µg/dL served as controls. No such effect was seen in M or in the combined analysis of M and F.	Sun et al. 2003
279 children, 9 mo–6 yrs old	General population	1–45 (range)	NM	Increased serum IgE	No other parameter of cellular or humoral immunity showed a significant association with PbB. Covariates: age, race, sex, nutrition, and SES.	Lutz et al. 1999
Neurological						
172 children, 5 yrs old	General population	7.7 (lifetime average)	NM	7.4 IQ points decline with PbB increase 1–10 µg/dL	Children tested with Stanford-Binet Intelligence Scale. Covariates: sex, birth-weight, iron status; mother's IQ, education, race, smoking, income, and HOME score.	Canfield et al. 2003a
4,853 children, 6–16 yrs old	General population	1.9 (geometric mean)	NM	PbB <5 µg/dL associated with decreased arithmetic and reading skills	Covariates: sex, race, iron status, exposure to second-hand smoke, region of the United States, marital status, country, parental education, poverty index, and birth weight. Exposure history was unknown.	Lanphear et al. 2000a

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
237 children, 7.5 yrs old	General population	5.4 (mean)	NM	PbB associated with decrements in domains of attention, executive function, visual-motor integration, social behavior and motor skills	Associations were present at PbB as low as 3 µg/dL; 19 variables were controlled for in addition to alcohol and drug use.	Chiodo et al. 2004
736 older adults	General population	4.5 (mean)	29.5 (mean patella)	Impaired cognitive test performance	Associations were found for both PbB and bone lead. Age, education, and alcohol intake were included in regression models.	Wright et al. 2003c
Reproductive						
74 adult men	Occupational	46.3 (mean)	NM	Decreased fertility	Wife's variables controlled for included parity, time since previous birth, age, birth cohort, employment status, and education. Husband's variables included smoking, alcohol intake, education, and parameters reflecting exposure intensity and duration.	Gennart et al. 1992b
251 men	Occupational	10-40 (range)	NM	Decreased fertility	Only couples with one pregnancy were included in study. Association existed only with younger maternal age (<30 years).	Sallmén et al. 2000b
121 women	General population	≥5.1 (cord blood)	NM	Increased pre-term births	The effect was evident only among primiparous, but not multiparous women.	Torres-Sánchez et al. 1999
Developmental						
329 infants, 1 mo old	General population	5.6 (mean)	15.3 (maternal patella)	PbB at 1 month and maternal patella bone inversely associated with weight gain	Infant age, sex, breast feeding practices, and infant health were included in regression models. Maternal variables: age, parity, maternal anthropometry, education, and hospital of recruitment.	Sanín et al. 2001

Population studied	Exposure	Blood lead (µg/dL)	Bone lead (ppm)	Effect	Comments	Reference
233 infants, 1 mo old	General population	7.0 (mean in cord blood)	14.1 (maternal patella)	Cord PbB associated with low birth length; patella lead associated with low head circumference	Variables included in models were maternal height, calf circumference, smoking, parity, reproductive history, age and education, hospital of delivery, infant sex, and gestational age.	Hernández-Avila et al. 2002
4,391 children, 1–7 yrs old	General population	1–72 (range)	NM	Reduced length or height and head circumference	Data from NHANES III. Models included: age, sex, ethnicity, and poverty-income ratio. Models also considered head of household education, exposure to cigarette smoke, nutrient intake, iron status, anemia, history of anemia, previous testing for high PbB, and previous treatment for lead poisoning.	Ballew et al. 1999
1,706 girls, 8–16 yrs old	General population	1–22 (range)	NM	Delayed sexual maturation	Data from NHANES III. Covariates: race/ ethnicity, age, family size, residence in metropolitan area, poverty-income ratio, and body mass index.	Wu et al. 2003b
2,741 girls, 8–18 yrs old	General population	3 (geometric mean)	NM	Delayed sexual maturation	Data from NHANES III. Covariates: age, height, body mass index, history of tobacco smoking or anemia, dietary intake of iron, vitamin C, calcium, and family income.	Selevan et al. 2003

ALAD = δ -aminolevulinic acid dehydratase; EKG = electrocardiogram; F = female(s); GFR glomerular filtration rate; HDL = high density lipoprotein; Ig = immunoglobulin; M = male(s); mo = month(s); NHANES III = Third National Health and Nutrition Examination; NM = not measured; SES = socioeconomic status; yr(s) = year(s)

Appendix B-1: Historical Data Request Form



DEPARTMENT OF THE AIR FORCE AIR UNIVERSITY (AETC)

9 Aug 05

MEMORANDUM FOR SGPB

FROM: AFIT/ENV

SUBJECT: SMALL ARMS FIRING RANGE DATA CALL

1. A research study on airborne exposures associated with leaded and lead-free (green) bullets is being initiated by the Department of Systems and Engineering Management. Request you provide data of all Bioenvironmental Engineering air sampling conducted at base firing range for the current range configuration. Purpose of this data call is to compile historical data of observations and air sampling results collected by base level Bioenvironmental Engineering Flight's across the Air Force. Results of this data call will help identify the different types of ammunition and ammunition traps being used as well as quantify the average inhalation exposure at Small Arms Ranges across the Air Force. In addition, it will assist current research efforts to identify different methods/techniques being used in the field to conduct air sampling at Small Arms Ranges. Techniques will serve as a starting point to develop a standardized methodology to collect future air sampling results. See attachment for specific firing range and air sampling results information being requested. Suspense Date: **9 Sep 05**.

2. This request has been coordinated by your MAJCOM BEE. If you have any questions regarding this request, please contact Capt Eric J. Cameron at eric.cameron@afit.edu. Thank you in advance for your time and effort on this data call. Your cooperation is greatly appreciated.

//Signed//

ERIC J. CAMERON, Capt, USAF, BSC
Bioenvironmental Engineer

Attachment:
Requested Small Arms Firing Range Information

1. Type of ammunition being fired: Lead-Free (Green) Bullets ☐ Lead ☐
Bullets

1a. Manufacturer: _____

1b. Caliber: _____

1c. CAS Number: _____

If "Green" Bullets being fired, please specify start date: _____

2. Type of Range at Installation (please include all ranges):

Enclosed ☐ Semi-Enclosed ☐ Open ☐ Mobile ☐

3. Type of trap being used to collect round:

☐ Hard Bullet Traps (e.g. metal to metal or Funnel Trap w/deceleration chamber)

☐ Soft Termination (e.g. earth or sand berm)

☐ Other: _____

In addition, please include the following:

☐ **All current air sampling results (Area and personal)**

- Please indicate whether lead or lead-free bullets fired at time of sampling

☐ Description of Firing Range (include pictures if available)

☐ Any special surveillance regarding inhalation exposure to instructor/shooters

☐ Latest Bioenvironmental Engineering Assessment

Appendix B-2: Human Subjects Board Approval Letter



DEPARTMENT OF THE AIR FORCE

AIR FORCE RESEARCH LABORATORY (AFRL)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

9 August 2005

MEMORANDUM FOR AFIT/ENV/GIR
ATTN: Eric J Cameron

FROM: AFRL/HEH

SUBJECT: Approval for the Use of Volunteers in Research.

1. Human experimentation as described in Protocol 05-54-E "A Comprehensive Look at Heavy Metal Exposure to Air Force Instructors and Shooters for Small Arms Ranges" may begin.
2. In accordance with AFI 40-402, this protocol was reviewed and approved by the Wright Site Institutional Review Board (WSIRB) on 20 July 2005, the AFRL Chief of Aerospace Medicine on 8 August 2005. A review is due 364 days from Board Review.
3. Please notify the undersigned of any changes in procedures prior to their implementation. A judgment will be made at that time whether or not a complete WSIRB review is necessary.

Signed 9 August 2005
HELEN JENNINGS
Human Use Administrator

Appendix B-3: Summary of Participating Bases and Collected Range Information

AMC	Type of Range			Type of Bullets		Type of Trap			Comments
	Indoor	Outdoor		Lead	Lead-Free	Hard Trap	Soft Trap		
		Semi-Enclosed	Open				Earth	Sand	
Davis Monthan AFB, AZ	-	-	X	X	-	-	X	-	
Barksdale AFB, LA	No data for base								
Beale AFB, CA	No data for base								
Cannon AFB, NM	No data for base								
Creech AFB, NV	No data for base								
Dyess AFB, TX	-	-	X	-	X	-	-	-	
Ellsworth AFB, SD	-	X	-	-	2004	X	-	-	-
Holloman AFB, NM	No data for base								
Langley AB, VA	-	-	X	Not identified					
Minot AFB, ND	-	X	-	X	-	X	-	-	Over OEL
Mountain Home AFB, ID	-	X	-	X *	X *	-	X	-	* Fire Both
Nellis AFB, NV	No data for base								
Offutt AFB, NE	No data for base								
Seymour Johnson AFB, NC	X	-	-	X	2004 only *	X	-	-	* Due to cost
Shaw AFB, SC	-	X	-	Not identified		X	-	-	
Whiteman AFB, MO	-	X	-	X	2005	-	X	-	
Altus AFB, OK	-	X	-	-	X	X	-	-	-
Columbus AFB, MS	No data for base								
Goodfellow AFB, TX	-	X	-	X	-	Not identified			No Air sampling data
Keesler AFB, MIS	-	-	X	-	Oct-05	-	X	-	
Lackland AFB, TX	-	X	-	Not identified					No Air sampling data

Laughlin AFB, TX	No data for base									
Little Rock AFB, AK	No data for base									
Luke AFB, AZ	No data for base									
Maxwell AFB, AL	-	X	-		X	X	-	-	-	
Randolph AFB, TX	No data for base									
Sheppard AFB, TX	No data for base									
Tyndall AFB, FL	-	X	-	X	-	X	-	-	-	
Vance AFB, OK	No data for base									
Arnold AFB, TN	No data for base									
Brooks City Base, TX	No data for base									
Edwards AFB, CA	-	-	X	-	X	-	X	-	-	
Eglin AFB, FL	No data for base									
Hanscom AFB, MAS	-	X	-	-	X	X	-	-	-	
Hill AFB, UT	X	-	-	-	2003	X	-	-	-	
Kirtland AFB, NM	-	X	-	-	X	X	-	-	-	
Robins AFB, GA	-	-	X	X	-	None				
Tinker AFB, OK	No data for base									
Wright-Patterson AFB, OH	2004	Prior 2004	-	-	2004	X	-	-		
Hurlburt AFB, FL	-	-	X	X	-	-	X	-		
Duke Field, FL	No data for bases									
Moody AFB, GA	-	-	X	-	X	-	X	-	-	
Buckley AFB, CO	-	-	X	X	-	-	X	-	-	
F.E. Warren AFB, WYO	X	-	-	Not identified						
Los Angeles AFB, CA	No data for bases									
Malstrom AFB, MA	-	X	-	-	2004	-	X	-	3 Ranges (2 open / 1 impact)	
Patrick AFB, FL	-	X	-	-	X	-	X	-	-	
Peterson AFB, CO	-	-	X	-	X	-	X	-	Shoot AF Academy	

Schrivier AFB, CO	No data for bases								
Vandenberg AFB, CA	-	-	X	-	X	-	-	X	-
Andrews AFB, MD	-	X	-	-	2000	Not Identified			
Charleston AFB, SC	-	-	X	-	X	X	-	-	-
Dover AFB, DE	-	X	-	X	-	Not Identified			
Fairchild AFB, WA	-	X	-	-	X	X	-	-	-
Grand Forks AFB, ND	-	X	-	-	2004	-	X	-	-
MacDill AFB, FL	-	X	-	-	X	X	-	-	-
McChord AFB, WA	No data for bases								
McConnel AFB, KA	No data for bases								
McGuire AFB, NJ	-	-	X	-	2002	-	X	-	-
Pope AFB, NC	No data for bases								
Scott AFB, IL	-	Since 97/98	Prior 97	-	X	Not Identified			
Travis AFB, CA	-	X	-	-	2004	Not Identified			
US AF Academy, CO	No data for bases								

Highlighted installations indicate repos received from initial data call

Appendix C: Material Safety Data Sheet for Lead-Free Ammunition



MATERIAL SAFETY DATA SHEET

Olin MSDS No.: 00085.0001	Revision Date: 1/1/05
Revision No.: 6	Supercedes: 1/1/04

1. PRODUCT AND COMPANY IDENTIFICATION

Product Name: CENTERFIRE LOADED ROUNDS, FRANGIBLE NON-TOXIC
Chemical Name: Mixture – Metal Alloy
Synonyms: 5.56 Frangible, Non-toxic, Sinterfire
Chemical Family: Metal mixture
Formula: Not applicable - mixture
Product Use: Centerfire Rifle and Pistol Loaded Ammunition

COMPANY ADDRESS	MSDS Control Group Olin Brass and Winchester, Inc. 427 North Shamrock St. East Alton, IL 62024-1197 www.winchester.com	TECHNICAL INFORMATION: 618-258-3507	EMERGENCY TELEPHONE NUMBER: 1-888-2891-911
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2. COMPOSITION/INFORMATION ON INGREDIENTS

CAS Number	Components	% By Weight	EINECS/ ELINCS #	EU Classification	
				Symbol	R-Phrase
7440-50-8	Copper	30 – 85	231-159-8	None	None
7440-86-8	Zinc	5 - 15	231-175-3	F (as dust or powder)	R15-17
7440-31-6	Tin	0.5 – 1.5	231-141-8	None	None
9004-70-0	Nitrocellulose	8 - 14	Not listed	E*	R 2
55-83-0	Nitroglycerin	0.5 - 2	200-240-8	E, T+, N	R3, R26/27/28, R33, R51-53

*This material is not listed in Annex 1 of Directive 88/379/EEC. Olin has classified the material according to the conventional method based upon information from similar materials.

OSHA REGULATORY STATUS: Explosive

3. HAZARDS IDENTIFICATION

CAUTION!	
EXPLOSIVE. KEEP AWAY FROM HEAT. DO NOT SUBJECT TO MECHANICAL SHOCK. PARTICLES FROM FIRING MAY BE HARMFUL IF INHALED. DO NOT TAKE INTERNALLY.	

HAZARD RATINGS (for dust or fume)
Hazardous Materials Identification System (HMIS)

Degree of hazard (0 = low, 4 = extreme)
 Health: 0 Flammability: 0

Physical Hazard:
 Explosive: 2

National Fire Protection Association (NFPA)

Mixture. Not rated.

HUMAN THRESHOLD RESPONSE DATA

Odor Threshold:

Unknown

Irritation Threshold:

Unknown

Immediately Dangerous to Life or Health (IDLH) Value(s):

The IDLH for this product is not known. The IDLH for copper is 100 mg/m³. The IDLH for nitroglycerin is 75 mg/m³.

POTENTIAL HEALTH EFFECTS

This product is composed of a finished metal alloy cartridge which contains the various components completely sealed within. Therefore, under normal handling of this product, no exposure to any harmful materials will occur.

When the ammunition is fired, a small amount of particles may be generated which may be slightly irritating to the eyes and the respiratory tract. The particles may contain trace amounts of these harmful substances:

MSDS # 00085.0001

Nitroglycerin: Will produce dilation of blood vessels and drop in blood pressure which may affect the heart. It has also been shown to cause methemoglobinemia (cyanosis).

Copper: Inhalation of high concentrations of metallic copper dusts or fumes may cause nasal irritation and/or nausea, vomiting and stomach pain.

It is unlikely that the amount of particles that someone would be exposed to from firing a loaded round would be sufficient to cause any of these effects.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE: There are no medical conditions known to be aggravated by exposure to this product in its solid form.

POTENTIAL ENVIRONMENTAL EFFECTS: None known.

4. FIRST AID MEASURES

EYE CONTACT: Immediately flush out fume or particles with large amounts of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. If eye irritation develops, call a physician at once.

SKIN CONTACT: Wash skin with plenty of soap and water.

INHALATION: If symptoms of lung irritation occur (coughing, wheezing or breathing difficulty), remove from exposure area to fresh air immediately. If breathing has stopped, perform artificial respiration. Keep affected person warm and at rest. Get medical attention.

INGESTION: If ingested, immediately call a physician.

5. FIRE FIGHTING MEASURES

PROPERTY	VALUE	PROPERTY	VALUE
Explosive	Yes	Flammable	Not applicable
Combustible	Not applicable	Pyrophoric	No
Flash Point (°C):	Not applicable	Burning Rate of Material:	Not applicable
Lower Explosive Limit:	Not applicable	Autoignition Temp.:	No data
Upper Explosive Limit:	Not applicable	Flammability Classification: (defined by 29 CFR 1910.1200)	Explosive

UNUSUAL FIRE AND EXPLOSION HAZARDS: If fire reaches cargo, do not fight. Evacuate all person, including emergency responders from the area for 1500 feet (1/3 mile) in all directions.

EXTINGUISHING MEDIA: Flood area with water. If no water is available, carbon dioxide, dry chemical or earth may be used. If the fire reaches the cargo, withdraw and let fire burn.

SPECIAL FIREFIGHTING PROCEDURES: In case of fire, use normal fire fighting equipment. Protection concerns must also address the potential of the physical characteristic of this product as explosive.

6. ACCIDENTAL RELEASE MEASURES

FOR ALL TRANSPORTATION ACCIDENTS, CALL CHEMTREC AT 800-424-9300.

Spills of this material should be handled carefully. Do not subject materials to mechanical shock. A spill of this material will normally not require emergency response team capabilities. If, however, a large spill occurs, call 1-888-289-1911 for technical assistance.

7. HANDLING AND STORAGE

HANDLING:

No special requirements

STORAGE:

No special requirements

Shelf Life Limitations:

Not known

Incompatible Materials for Packaging:

None known

Incompatible Materials for Storage or Transport:

Acids, Class A & B explosives, strong oxidizers, and caustics

CONDITIONS TO AVOID:

Mechanical impact or shock and electrical discharge.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

CAS #	CHEMICAL NAME	ACGIH TLV	OSHA PEL	INTERNATIONAL OELS
7440-50-8	Copper	0.2 mg/m ³ (fume), 1 mg/m ³ (dusts and mists)	0.1 mg/m ³ (fume) 1 mg/m ³ (dusts and mists)	Austria, Belgium, Canada: 0.2 mg/m ³ (fumes), 1 mg/m ³ (dusts) Denmark: 1.0 mg/m ³ (dust and powder) Germany (MAK): 0.1 mg/m ³ (fume), 1 mg/m ³ (dusts and mists)
7440-86-8	Zinc	None established	None established	None established
7440-31-6	Tin	2 mg/m ³	2 mg/m ³	None established
9004-70-0	Nitrocellulose	None established	None established	None established
56-83-0	Nitroglycerin	0.05 ppm (0.48 mg/m ³) Skin	Ceiling – 0.2 ppm (2 mg/m ³) Skin	Denmark: 0.02 ppm (0.2 mg/m ³) Norway, Sweden: 0.03 ppm (0.3 mg/m ³) Austria, Belgium, Germany, The Netherlands, Poland, Switzerland: 0.05 ppm (0.47 mg/m ³), skin Finland, France: 0.1 ppm (0.9 mg/m ³), skin U.K.: 0.2 ppm (2 mg/m ³), skin

ENGINEERING CONTROLS: Local exhaust ventilation is recommended if significant dusting occurs or fumes are generated. Otherwise, use general exhaust ventilation. Use hearing protection.

EYE / FACE PROTECTION: Use safety glasses.

SKIN PROTECTION: Not normally needed.

RESPIRATORY PROTECTION: Respiratory protection not normally needed.

GENERAL HYGIENE: Do not eat, drink, or smoke while using this product. Wash hands thoroughly after use.

9. PHYSICAL AND CHEMICAL PROPERTIES

PROPERTY	VALUE	PROPERTY	VALUE
Appearance:	Cylindrical brass cartridge	Vapor Density (air = 1):	Not applicable
Odor:	None	Boiling Point (°F):	Not applicable
Molecular Weight:	Not applicable - Mixture	Melting point:	Not applicable
Physical State:	Solid	Specific gravity (g/cc):	Not applicable
pH:	Not applicable	Bulk Density:	Not applicable
Vapor Pressure (mm Hg):	Not applicable	Viscosity (cps):	Not applicable
Vapor Density:	Not applicable	Decomposition Temperature:	Not applicable
Solubility in Water (20 °C):	Insoluble	Evaporation Rate:	Not applicable
Volatiles, Percent by volume:	Not applicable	Octanol/water partition coefficient:	Not applicable

10. STABILITY AND REACTIVITY

STABILITY: Stable under normal temperatures and pressure.

MATERIALS TO AVOID: Acids, Class A & B explosives, strong oxidizers, and caustics.

HAZARDOUS DECOMPOSITION PRODUCTS: Nitrogen oxides, carbon monoxide, carbon dioxide.

HAZARDOUS POLYMERIZATION: Will not occur.

OTHER: Cartridge may detonate if case is punctured or severely damaged.

11. TOXICOLOGICAL INFORMATION

POTENTIAL EXPOSURE ROUTES: The physical nature of this product makes absorption from any route unlikely. A small amount of inhalable particles may be created when projectile is fired.

ACUTE ANIMAL TOXICITY DATA:

For Product:		For Components				
		Copper	Tin	Nitrocellulose	Zinc	Nitroglycerin
Oral LD ₅₀	Not applicable for product	3.5 mg/kg (mouse, intraperitoneal)	No data	> 5 g/kg (rat)	No data	105 mg/kg (rat)
Dermal LD ₅₀	Not applicable for product	375 mg/kg (rabbit, subcutaneous)	No data	No data	No data	> 280 mg/kg (rabbit)

MSDS No.: 00085.0001

For Product:		For Components				
		Copper	Tin	Nitrocellulose	Zinc	Nitroglycerin
Inhalation LC ₅₀	Not applicable for product. Particles generated from firing may be slightly toxic.	No data	No data	No data	No data	No data
Irritation	Not a skin or eye irritant as a loaded round.	Respiratory irritant	No data	No data	Eye irritant	Mild eye and skin irritant

SUBCHRONIC/ CHRONIC TOXICITY:
CARCINOGENICITY:

No information for product.
This product or its components are not classified as carcinogenic by IARC, NTP, OSHA or EPA.

MUTAGENICITY:
REPRODUCTIVE, TERATOGENICITY, OR DEVELOPMENTAL EFFECTS:
NEUROLOGICAL EFFECTS:
INTERACTIONS WITH OTHER CHEMICALS WHICH ENHANCE TOXICITY:

This product is not known or reported to be mutagenic.
This product is not known or reported to cause reproductive or developmental effects.
This product is not known or reported to cause neurological effects.

None known or reported.

12. ECOLOGICAL INFORMATION

ECOTOXICITY: No data is available on this product. Individual constituents are as follows:

Copper: The toxicity of copper to aquatic organisms varies significantly not only with the species, but also with the physical and chemical characteristics of the water, such as its temperature, hardness, turbidity and carbon dioxide content. Copper concentration varying from 0.1 to 1.0 mg/l have been found by various investigators to be not toxic for most fish. However, concentrations of 0.015 to 3.0 mg/l have been reported as toxic, particularly in soft water to many kinds of fish, crustacea, mollusks, insects, and plankton.

Nitrocellulose: LC₅₀ > 1000 mg/l (fish, invertebrates, algae)

Nitroglycerin: Bluegill, 96 hour LC₅₀ = 1,228 mg/l (static)

Zinc: The following concentrations of zinc have been reported as lethal to fish:

Rainbow trout fingerlings: 0.13 mg/l, 12 – 24 hours
Bluegill sunfish: 6 hr TLM = 1.9 – 3.6 mg/l (soft water, 30°C)
Rainbow trout: 4 mg/l (hard water) 3 days
Sticklebacks: 1 mg/l (soft water) 24 hrs

The presence of copper appears to have a synergistic effect on the toxicity of zinc towards fish.

MOBILITY: No data

PERSISTENCE/DEGRADABILITY: Not biodegradable. Bullets may fragment and decompose in soil.

BIOACCUMULATION: No data

13. DISPOSAL CONSIDERATIONS

Care must be taken to prevent environmental contamination from the use of this material. The user of this material has the responsibility to dispose of unused material, residues and containers in compliance with all relevant local, state and federal laws and regulations regarding treatment, storage and disposal for hazardous and nonhazardous wastes.

14. TRANSPORT INFORMATION

	U.S. DOT	RID/ADR	IMDG	IATA	IMO	Canada TDG
PROPER SHIPPING NAME:	Cartridges, small arms					
HAZARD CLASS:	1.4S					
UN NO.:	UN 0012					
PACKING GROUP:	II					
HAZARD LABEL/PLACARD:	No label required highway/water 1.4S Label Air/ 1.4 Placard over 1001 lbs. (454 kg)					
REPORTABLE QUANTITY:	Not applicable					

SPECIAL COMMENTS:	May be reclassified domestically (U.S. Land) as an ORM-D if packaged as per 49 CFR 173.63. Mark ORM-D per 49 CFR 172.316.	
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15. REGULATORY INFORMATION

US FEDERAL

TSCA:	The components of this product are listed on the Toxic Substance Control Act inventory.				
CERCLA:	Copper, R.Q. = 6000 lbs.; Zinc, R.Q. = 1000 lbs.; Nitroglycerin, R.Q. = 10 lbs. (No reporting is required if diameter of the pieces of metal is equal to or exceeds 100 micrometers (0.004 inches)).				
SARA 313:	Copper, Zinc (fume or dust), Nitroglycerin				
SARA 313 Hazard Class:	Health: For dust or fume only	Acute - Yes, Chronic - Yes	Fire: None	Reactivity: None	Release of Pressure: None
SARA 302 EHS List:	None of the components of this product are listed.				

RQ = Reportable Quantity

STATE RIGHT-TO-KNOW STATUS

Component	*CA Prop. 65	New Jersey	Pennsylvania	Massachusetts	Michigan
Copper	Not listed	X	X	X	X
Zinc	Not listed	X	Not listed	X	X
Tin	Not listed	Not listed	X	X	Not listed
Nitrocellulose	Not listed	X	X	X	Not listed
Nitroglycerin	Not listed	X	X	X	Not listed

EUROPEAN REGULATIONS

Hazard Classification

Danger Symbol:	E	Explosive
Risk Phrases:	R2	Risk of explosion by shock, friction, fire or other sources of ignition
Safety Phrases:	S2	Keep out of reach of children.

German WGK Classification: Unknown.

CANADIAN REGULATIONS

DSL LIST: The components of this product are on the DSL or are exempt from reporting under the New Substances Notification Regulations.
IDL: Copper, Tin
WHMIS: This product is not subject to WHMIS. It is regulated as a Class 6 Explosive in Canada.

16. OTHER INFORMATION

REVISIONS:

PREPARED BY: Olin Corporation

OTHER: Additional information available from: www.winchester.com

NOTICE: THE INFORMATION IN THIS MSDS SHOULD BE PROVIDED TO ALL WHO WILL USE, HANDLE, STORE, TRANSPORT, OR OTHERWISE BE EXPOSED TO THIS PRODUCT. THIS INFORMATION HAS BEEN PREPARED FOR THE GUIDANCE OF PLANT ENGINEERING, OPERATIONS AND MANAGEMENT AND FOR PERSONS WORKING WITH OR HANDLING THIS PRODUCT. OLIN BELIEVES THIS INFORMATION TO BE RELIABLE AND CURRENT AS OF THE DATE OF PUBLICATION, BUT MAKES NO WARRANTY THAT IT IS.

MATERIAL SAFETY DATA SHEET

**SMALL ARMS AMMUNITION
BALLISTIC CLEAN 5.56MM
CENTERFIRE RIFLE AMMUNITION**

Federal Cartridge Company
900 Ehlen Drive
Anoka, Minnesota 55303

TELEPHONE: 763-323-2300
PRODUCT SERVICE: 763-323-3706
EMERGENCY PHONE NUMBER: 800-424-9300 (CHEMTREC)

Issue Date: August 19, 2003

SECTION #1 - PRODUCT IDENTIFICATION:

NON-TOXIC CENTERFIRE RIFLE PRODUCT FAMILY		
Centerfire Metallic Cartridge Including The Following:		
BC556NT1		

SECTION #2 - CHEMICAL COMPOUNDS:

CHEMICAL COMPOUNDS			
	CAS NUMBER	TWA UNLESS OTHERWISE NOTED	
		OSHA PEL	ACGIH TLV
Bullet *Copper Jacket	7440-50-8	1 mg/m ³ Fume: .1 mg/m ³	1 mg/m ³ Fume: .2 mg/m ³
Core: Copper Powder (See Above)			
Zytel Nylon	None Assigned	15 mg/m ³ (5 mg/m ³ as respirable dust)	15 mg/m ³ (5 mg/m ³ as respirable dust)
Cartridge Case - Brass (As Copper) (See above)			
* Zinc (As Zinc Oxide)	7440-66-6 1314-13-2	10 mg/m ³ (5 mg/m ³ as respirable dust) Fume: 5 mg/m ³	10 mg/m ³ Fume: 5 mg/m ³
Propellant - Nitrocellulose	9004-70-0	Not Established	Not Established
*Nitroglycerine	55-63-0	.1 mg/m ³ STEL	.46 mg/m ³ (Skin)
Diphenylamine	122-39-4	Not Established	10 mg/m ³
Primer - Diazodinitrophenol	87-31-0	Not Established	Not Established
Tetracene	109-27-3	Not Established	Not Established
* Barium Nitrate (As Barium)	7440-39-3	.5 mg/m ³	.5 mg/m ³
*Aluminum	7429-90-5	15 mg/m ³ (5 mg/m ³ as respirable dust)	10 mg/m ³
Nitrocellulose (See above)			
Nitroglycerine (See above)			

* Indicates toxic chemical(s) subject to the reporting requirements of section 313 of title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 and 40 CFR 372.

DEFINITIONS OF ACRONYMS

OSHA PEL:	Occupational Safety and Health Administration's Permissible Exposure Limit.
ACGIH TLV:	American Conference of Governmental Industrial Hygienists' Threshold Limit Values.
TWA:	Time Weighted Average.
STEL:	Short Term Exposure Limit, the 15-minute exposure that should not be exceeded at any time during a workday.
CEILING:	The concentration that is not to be exceeded at any time during a workday.
CAS:	Chemical Abstracts Service number.

SECTION #3 - PHYSICAL DATA

Boiling Point:	Not Applicable
Melting Point:	Not Applicable
Vapor Pressure:	Not Applicable
Density:	3.1 - 8.0 grams/cc
Solubility (Water):	None
Evaporation Rate:	Not Applicable
Percent Volatiles:	Not Applicable
Vapor Density (Air = 1):	Not Applicable
Appearance:	Brass case with copper/Zytel nylon bullet.
Odor:	None
Odor Threshold:	None

SECTION #4 - FIRE FIGHTING & EXPLOSION DATA:

Flash Point (F):	Not Applicable
Auto Ignition Temperature (F):	Not Applicable
Upper Explosive Limits (Percent):	Not Applicable
Lower Explosive Limits (Percent):	Not Applicable
Fire & Explosion Hazards:	May ignite if heated to 250 degrees F, independent of air. Unconfined ignited cartridges can produce low velocity metallic fragments that may cause eye injury or superficial skin wounds if unprotected by standard fire-fighter turnout gear.
Extinguishing Media:	Water
Special Fire Fighting Instructions:	Wear full fire-fighter protective gear including face shield or SCBA. Use wide fog pattern nozzle to stop any low velocity fragments. Use water to cool ordinary combustibles below ignition temperature.

SECTION #5A - EXPOSURE & EFFECTS -- INHALATION

ROUTE OF EXPOSURE & EFFECTS - INHALATION

Acute: Acute inhalation of smoke may produce mild throat and eye irritations.

Chronic: None known.

First Aid: Remove person to fresh air. If breathing has stopped, administer artificial respiration. If symptoms should appear, contact physician.

SECTION #5B - EXPOSURE & EFFECTS -- SKIN

ROUTES OF EXPOSURE & EFFECTS - SKIN

Acute: Contact with metal fumes may cause skin irritation.

Chronic: None known.

First Aid: Wash thoroughly with soap and water.

SECTION #5C - EXPOSURE & EFFECTS -- EYES

ROUTES OF EXPOSURE & EFFECTS - EYES

Acute: Contact with large volumes of smoke may cause minor eye irritation.

Chronic: None known.

First Aid: Remove person to fresh air. If foreign body is suspected, wash eyes in fresh water for 15 minutes, contact physician.

SECTION #5D - EXPOSURE & EFFECTS -- INGESTION

ROUTE OF EXPOSURE & EFFECTS - INGESTION

Acute: Ingestion of nitroglycerin is known to cause headaches, convulsions, tachycardia and apnea. Ingestion is not a likely route of exposure.

Chronic: None known.

Note: Wash hands thoroughly with soap and water before eating or smoking.

First Aid: Ingestion is not a likely route of exposure. In case of ingestion, contact physician.

SECTION #5E - EXPOSURE & EFFECTS -- CARCINOGENESIS DATA

N.T.P.: No

I.A.R.C.: No

OSHA: No

SECTION #5F - EXPOSURE & EFFECTS - COMMENTS

Barium is a toxic metal, at high concentrations. Ballisticlean ammunition contains trace levels of Barium.

SECTION #5G - AGGRAVATION OF PRE-EXISTING HEALTH CONDITIONS

AGGRAVATION TO PRE-EXISTING HEALTH CONDITIONS

None known.

SECTION #6 - REACTIVITY & POLYMERIZATION

Stability: Stable under normal use conditions.

Conditions to Avoid: Individual cartridges may ignite if the primer is struck or if the cartridge is exposed to excess heat.

Incompatible Materials: Oils, Acids, Alkalies, Ammonia, and other corrosive materials.

Hazardous Decomposition Materials: Oxides of Barium, Nitrogen and Carbon.

Polymerization: Will not occur.

SECTION #7 - SPILLS, LEAKS & DISPOSAL PROCEDURES

STEPS TO BE TAKEN - SPILLS:

Avoid conditions detailed in Section #6. If container should rupture place all loose cartridges from broken shipping cases into a sturdy container, secure container carefully.

Waste Disposal Methods: Contact Manufacturer - Product Service (763) 323-3706.

SECTION #8 - SPECIAL PROTECTIVE EQUIPMENT

Ventilation: Use in a well-ventilated area. Consult the current edition of ACGIH Industrial Ventilation Manual and/or NRA ventilation recommendations.

Protective Equipment:

Eyes: Recommend protective eyewear conforming to ANSI Z-87.

Gloves: Not generally required.

Respirators: Use an approved respirator while cleaning range facilities if applicable exposure limits are exceeded.

Hearing Protection: Hearing protection recommended while discharging cartridges.

SECTION #9 - SPECIAL PRECAUTIONS – STORAGE & HANDLING

Store in a dry, cool area in the original container to assure performance. Keep out of the reach of children. Avoid striking the primer of unchambered cartridges. Remove ammunition from service if any of the following conditions have occurred:

1. Prolonged storage at or above 170 degrees F.
2. Evidence of corrosion.
3. Physical damage.
4. Exposure to oil or spray type lubricants.

Avoid prolonged storage in leather cartridge carriers. Cartridges can ignite if heated to 250 degrees F independent of air.

SECTION #10 – TRANSPORTATION INFORMATION

This material is a US Department of Transportation Hazardous Material.

US DOT Proper Shipping Name:	Cartridges, small arms
Hazard Classification:	1.4S
UN Identification Number:	UN0012
Packing Group:	II

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Although reasonable care has been taken in the preparation of this document, Federal Cartridge Company extends no warranties and makes no representation as to the accuracy or completeness of the information contained herein and assumes no responsibility regarding the suitability of this information for the user's intended purpose or the consequences of its use. Each individual should make a determination as to the suitability of the information for their particular purpose.

Appendix D-1: Analytical Air Sampling Results from Hill AFB

Analytical Results
for
U.S. AIR FORCE
Work Order No.: 05100009
Client Reference: F41622-02-A0001/HILL AFB/

Sample Type: NH3 Tube
Method Reference: Ammonia; Method: NIOSH S-347
Date Received: 10/03/2005
Analyst: CLH
RL (µg): 20

Lab No.	Sample Identification	Air Volume (liters)	Ammonia			Date Analyzed
			(µg)	(mg/m³)	(ppm)	
001A	BK054556 BLANK 09/21/05	0	<20	--	--	10/10/2005
002A	BK054557 BLANK 09/21/05	0	<20	--	--	10/10/2005
003A	SZ054558 09/21/05	30.1444	<20	<0.66	<0.95	10/10/2005
004A	SZ054559 09/21/05	31.0464	<20	<0.64	<0.92	10/10/2005
005A	SZ054560 09/21/05	21.2628	<20	<0.94	<1.4	10/10/2005
006A	BK054571 BLANK 09/23/05	0	<20	--	--	10/10/2005
007A	BK054572 BLANK 09/23/05	0	<20	--	--	10/10/2005
008A	SZ054573 09/23/05	24.3741	<20	<0.82	<1.2	10/10/2005
009A	SZ054574 09/23/05	24.7408	<20	<0.81	<1.2	10/10/2005
010A	SZ054575 09/23/05	13.764	<20	<1.5	<2.1	10/10/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

**Analytical Results
for
U.S. AIR FORCE
Work Order No.: 05100009
Client Reference: F41622-02-A0001/HILL AFB/**

Sample Type: HCN Tube **Date Received:** 10/03/2005
Method Reference: NIOSH 6010 **Analyst:** MP
RL (µg): 2.4

Lab No.	Sample Identification	Air Volume (liters)	Hydrogen Cyanide			Date Analyzed
			(µg)	(mg/m ³)	(ppm)	
011A	BK054561 BLANK 09/21/05	0	<2.4	--	--	10/05/2005
012A	BK054562 BLANK 09/21/05	0	<2.4	--	--	10/05/2005
013A	SZ054563 09/21/05	17.8494	<2.4	<0.13	<0.12	10/05/2005
014A	SZ054564 09/21/05	18.1324	<2.4	<0.13	<0.12	10/05/2005
015A	SZ054565 09/21/05	17.9211	<2.4	<0.13	<0.12	10/05/2005
016A	BK054576 BLANK 09/23/05	0	<2.4	--	--	10/05/2005
017A	BK054577 BLANK 09/23/05	0	<2.4	--	--	10/05/2005
018A	SZ054578 09/23/05	13.9219	<2.4	<0.17	<0.16	10/05/2005
019A	SZ054579 09/23/05	14.2464	<2.4	<0.17	<0.15	10/05/2005
020A	SZ054580 09/23/05	13.7418	<2.4	<0.17	<0.16	10/05/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

**Analytical Results
for**

U.S. AIR FORCE

Clayton Work Order No.: 05100091

Client Reference: F41622-02-A0001/HILL

Client ID:	BK054551	Date Sampled:	9/21/2005
Lab ID:	001A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol(L):	NA

Analyte	Concentration (µg)	Concentration (mg/m³)	Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	--	1	NIOSH 7300	10/06/2005	DH
Copper	<1	--	1	NIOSH 7300	10/06/2005	DH
Lead	<1	--	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	--	1	NIOSH 7300	10/06/2005	DH
Tin	<1	--	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	--	1	NIOSH 7300	10/06/2005	DH

Client ID:	BK054552 BLANK	Date Sampled:	9/21/2005
Lab ID:	002A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol(L):	NA

Analyte	Concentration (µg)	Concentration (mg/m³)	Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	--	1	NIOSH 7300	10/06/2005	DH
Copper	<1	--	1	NIOSH 7300	10/06/2005	DH
Lead	<1	--	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	--	1	NIOSH 7300	10/06/2005	DH
Tin	<1	--	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	--	1	NIOSH 7300	10/06/2005	DH

**Analytical Results
for**

U.S. AIR FORCE

Clayton Work Order No.: 05100091

Client Reference: F41622-02-A0001/HILL

Client ID:	SZ054553	Date Sampled:	9/21/2005
Lab ID:	003A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	162.162

Analyte	Concentration		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
	(µg)	(mg/m³)				
Barium	<1	<0.0062	1	NIOSH 7300	10/06/2005	DH
Copper	2.6	0.016	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0062	1	NIOSH 7300	10/06/2005	DH
Nickel	3.8	0.024	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0062	1	NIOSH 7300	10/06/2005	DH
Zinc	5.9	0.036	1	NIOSH 7300	10/06/2005	DH

Client ID:	SZ054554	Date Sampled:	9/21/2005
Lab ID:	004A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	167.475

Analyte	Concentration		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
	(µg)	(mg/m³)				
Barium	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH
Copper	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	<0.0060	1	NIOSH 7300	10/06/2005	DH

**Analytical Results
for**

U.S. AIR FORCE

Clayton Work Order No.: 05100091

Client Reference: F41622-02-A0001/HILL

Client ID:	SZ054555	Date Sampled:	9/21/2005
Lab ID:	005A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol(L):	136.2765

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH
Copper	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	<0.0073	1	NIOSH 7300	10/06/2005	DH

Client ID:	BK054566 BLANK	Date Sampled:	9/23/2005
Lab ID:	006A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol(L):	NA

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	--	1	NIOSH 7300	10/06/2005	DH
Copper	<1	--	1	NIOSH 7300	10/06/2005	DH
Lead	<1	--	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	--	1	NIOSH 7300	10/06/2005	DH
Tin	<1	--	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	--	1	NIOSH 7300	10/06/2005	DH

**Analytical Results
for**

U.S. AIR FORCE

Clayton Work Order No.: 05100091

Client Reference: F41622-02-A0001/HILL

Client ID:	BK054567 BLANK	Date Sampled:	9/23/2005
Lab ID:	007A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	NA

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	--	1	NIOSH 7300	10/06/2005	DH
Copper	<1	--	1	NIOSH 7300	10/06/2005	DH
Lead	<1	--	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	--	1	NIOSH 7300	10/06/2005	DH
Tin	<1	--	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	--	1	NIOSH 7300	10/06/2005	DH

Client ID:	SZ054568	Date Sampled:	9/23/2005
Lab ID:	008A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	123.17

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH
Copper	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	<0.0081	1	NIOSH 7300	10/06/2005	DH

**Analytical Results
for**

U.S. AIR FORCE

Clayton Work Order No.: 05100091

Client Reference: F41622-02-A0001/HILL

Client ID:	SZ054569	Date Sampled:	9/23/2005
Lab ID:	009A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	128.8

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH
Copper	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	<0.0078	1	NIOSH 7300	10/06/2005	DH

Client ID:	SZ054570	Date Sampled:	9/23/2005
Lab ID:	010A	Date Received:	10/4/2005
Matrix:	MCE Filter, .8um	Air Vol.(L):	154.254

Analyte	Concentration (µg) (mg/m³)		Reporting Limit (µg)	Test Method	Date Analyzed/Analyst	
Barium	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH
Copper	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH
Lead	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH
Nickel	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH
Tin	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH
Zinc	<1	<0.0065	1	NIOSH 7300	10/06/2005	DH

General Notes:

<: Less than the indicated reporting limit (RL).
--: Information not available or not applicable.

ANALYTICAL RESULTS

Date: 23-Nov-05

Client: U.S. AIR FORCE
Project: F41622-02-A0001/HILL AFB UTAH
Sample Type: NH3 Tube
Method Reference: NIOSH S-347
RL (µg): 20

Work Order No: 05110711
Date Received: 11/15/2005
Analyst: CLH

Lab No.	Sample Identification	Air Volume (liters)	Ammonia			Date Analyzed
			(µg)	(mg/m³)	(ppm)	
006A	BK054860 BLANK 11/01/05	0	<20	--	--	11/22/2005
007A	BK054861 BLANK 11/01/05	0	<20	--	--	11/22/2005
008A	SZ054862 11/01/05	21.5017	<20	<0.93	<1.3	11/22/2005
009A	SZ054863 11/01/05	25.0992	<20	<0.80	<1.1	11/22/2005
010A	SX054864 11/01/05	25.2125	<20	<0.79	<1.1	11/22/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

ANALYTICAL RESULTS

Date: 23-Nov-05

Client: U.S. AIR FORCE
Project: F41622-02-A0001/HILL AFB UTAH
Sample Type: HCN Tube
Method Reference: NIOSH 6010
RL (µg): 2.4

Work Order No: 05110711
Date Received: 11/15/2005
Analyst: CLH

Lab No.	Sample Identification	Air Volume (liters)	Hydrogen Cyanide			Date Analyzed
			(µg)	(mg/m³)	(ppm)	
001A	BK054865 BLANK 11/01/05	0	<2.4	--	--	11/18/2005
002A	BK054866 BLANK 11/01/05	0	<2.4	--	--	11/18/2005
003A	SZ054867 11/01/05	15.3598	<2.4	<0.16	<0.14	11/18/2005
004A	SZ054868 11/01/05	15.4	<2.4	<0.16	<0.14	11/18/2005
005A	SX054869 11/01/05	15.3388	<2.4	<0.16	<0.14	11/18/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

**Air Metals Report of Analysis
for**

75 AMDS/SCPB

WorkOrder: S0511183

Project:

Date Reported: 12/02/2005

Client Sample ID: BK054855	Date Sampled: 11/1/2005
Lab Sample ID: S0511183-01A	Date Received: 11/14/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0340	Approver: Juanita Gilliland
Sample Location: BLDG 741	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/28/2005 10:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Barium	<0.250	—	—	0.250	1	11/29/2005 4:35:59 PM	JMM
Copper	<1.25	—	—	1.25	1	11/29/2005 4:35:59 PM	JMM
Lead	<0.625	—	—	0.625	1	11/29/2005 4:35:59 PM	JMM
Nickel	<0.625	—	—	0.625	1	11/29/2005 4:35:59 PM	JMM
Zinc	<1.25	—	—	1.25	1	11/29/2005 4:35:59 PM	JMM

Client Sample ID: BK054856	Date Sampled: 11/1/2005
Lab Sample ID: S0511183-02A	Date Received: 11/14/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0340	Approver: Juanita Gilliland
Sample Location: BLDG 741	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/28/2005 10:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Barium	<0.250	—	—	0.250	1	11/29/2005 4:39:08 PM	JMM
Copper	<1.25	—	—	1.25	1	11/29/2005 4:39:08 PM	JMM
Lead	<0.625	—	—	0.625	1	11/29/2005 4:39:08 PM	JMM
Nickel	<0.625	—	—	0.625	1	11/29/2005 4:39:08 PM	JMM
Zinc	<1.25	—	—	1.25	1	11/29/2005 4:39:08 PM	JMM

Air Metals Report of Analysis for

75 AMDS/SGPB

WorkOrder: S0511183

Project:

Date Reported: 12/02/2005

Client Sample ID: SZ054857	Date Sampled: 11/1/2005
Lab Sample ID: S0511183-03A	Date Received: 11/14/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): 139.974	
Site Identifier: 0340	Approver: Juanita Gilliland
Sample Location: BLDG 741	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/28/2005 10:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Barium	<0.250	<0.00179	—	0.250	1	11/29/2005 4:42:09 PM	JMM
Copper	<1.25	<0.00893	—	1.25	1	11/29/2005 4:42:09 PM	JMM
Lead	<0.625	<0.00447	—	0.625	1	11/29/2005 4:42:09 PM	JMM
Nickel	<0.625	<0.00447	—	0.625	1	11/29/2005 4:42:09 PM	JMM
Zinc	<1.25	<0.00893	—	1.25	1	11/29/2005 4:42:09 PM	JMM

Client Sample ID: SZ054858	Date Sampled: 11/1/2005
Lab Sample ID: S0511183-04A	Date Received: 11/14/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): 143.51	
Site Identifier: 0340	Approver: Juanita Gilliland
Sample Location: BLDG 741	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/28/2005 10:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Barium	<0.250	<0.00174	—	0.250	1	11/29/2005 4:45:12 PM	JMM
Copper	<1.25	<0.00871	—	1.25	1	11/29/2005 4:45:12 PM	JMM
Lead	<0.625	<0.00436	—	0.625	1	11/29/2005 4:45:12 PM	JMM
Nickel	<0.625	<0.00436	—	0.625	1	11/29/2005 4:45:12 PM	JMM
Zinc	<1.25	<0.00871	—	1.25	1	11/29/2005 4:45:12 PM	JMM

Air Metals Report of Analysis for

75 AMDS/SGPB

WorkOrder: S0511183

Project:

Date Reported: 12/02/2005

Client Sample ID: SX054859	Date Sampled: 11/1/2005
Lab Sample ID: S0511183-05A	Date Received: 11/14/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): 141.081	
Site Identifier: 0340	Approver: Juanita Gilliland
Sample Location: BLDG 741	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/28/2005 10:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Barium	<0.250	<0.00177	—	0.250	1	11/29/2005 4:48:20 PM	JMM
Copper	<1.25	<0.00886	—	1.25	1	11/29/2005 4:48:20 PM	JMM
Lead	<0.625	<0.00443	—	0.625	1	11/29/2005 4:48:20 PM	JMM
Nickel	<0.625	<0.00443	—	0.625	1	11/29/2005 4:48:20 PM	JMM
Zinc	<1.25	<0.00886	—	1.25	1	11/29/2005 4:48:20 PM	JMM

General Notes:

<: Less than the indicated limit of detection (LOD).

—: Information not available or not applicable.

The calculated concentration (mg/m³) was obtained using the collection volume provided on the analysis request form.

Appendix D-2: Analytical Air Sampling Results from McGuire AFB

ANALYTICAL RESULTS

Date: 02-Dec-05

Client: U.S. AIR FORCE
 Project: F41622-02-A0001/McGUIRE AFB/
 Sample Type: NH3 Tube
 Method Reference: NIOSH S-347
 RL (µg): 20

Work Order No: 05111147
 Date Received: 11/23/2005
 Analyst: RAS

Lab No.	Sample Identification	Air Volume (liters)	Ammonia			Date Analyzed
			(µg)	(mg/m³)	(ppm)	
001A	BK050507 BLANK 11/02/05	0	<20	--	--	11/30/2005
002A	BK050508 BLANK 11/02/05	0	<20	--	--	11/30/2005
003A	SZ050509 11/02/05	30.5732	<20	<0.65	<0.94	11/30/2005
004A	SZ050510 11/02/05	32.4198	<20	<0.62	<0.89	11/30/2005
005A	SZ050511 11/02/05	29.725	<20	<0.67	<0.97	11/30/2005
006A	BK050522 BLANK 11/03/05	0	<20	--	--	11/30/2005
007A	BK050523 BLANK 11/03/05	0	<20	--	--	11/30/2005
008A	SZ050524 11/03/05	20.752	<20	<0.96	<1.4	11/30/2005
009A	SZ050525 11/03/05	19.8588	<20	<1.0	<1.4	11/30/2005
010A	SZ050526 11/03/05	14.7494	<20	<1.4	<1.9	11/30/2005
011A	BK050546 BLANK 11/15/05	0	<20	--	--	11/30/2005
012A	SZ050547 11/15/05	20.2338	<20	<0.99	<1.4	11/30/2005
013A	SZ050548 11/15/05	2.0048	<20	<1.0	<1.4	11/30/2005
014A	SZ050549 11/15/05	18.315	<20	<1.1	<1.6	11/30/2005
015A	BK050558 BLANK 11/15/05	0	<20	--	--	11/30/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

ANALYTICAL RESULTS

Date: 02-Dec-05

Client: U.S. AIR FORCE
 Project: F41622-02-A0001/McGUIRE AFB/
 Sample Type: HCN Tube
 Method Reference: NIOSH 6010
 RL (µg): 2.4

Work Order No: 05111146
 Date Received: 11/23/2005
 Analyst: CLH

Lab No.	Sample Identification	Air Volume (liters)	Hydrogen Cyanide			Date Analyzed
			(µg)	(mg/m³)	(ppm)	
001A	BK050512 BLANK 11/02/05	0	<2.4	--	--	11/28/2005
002A	BK050513 BLANK 11/02/05	0	<2.4	--	--	11/28/2005
003A	SZ050514 11/02/05	21.6428	<2.4	<0.11	<0.10	11/28/2005
004A	SZ050515 11/02/05	21.9744	<2.4	<0.11	<0.099	11/28/2005
005A	SZ050516 11/02/05	21.9625	<2.4	<0.11	<0.099	11/28/2005
006A	BK050527 BLANK 11/03/05	0	<2.4	--	--	11/28/2005
007A	BK050528 BLANK 11/03/05	0	<2.4	--	--	11/28/2005
008A	SZ050529 11/03/05	13.816	<2.4	<0.17	<0.16	11/28/2005
009A	SZ050530 11/03/05	9.8774	<2.4	<0.24	<0.22	11/28/2005
010A	SZ050531 11/03/05	9.976	<2.4	<0.24	<0.22	11/28/2005
011A	BK050550 BLANK 11/15/05	0	<2.4	--	--	11/28/2005
012A	BK050551 BLANK 11/15/05	0	<2.4	--	--	11/28/2005
013A	SZ050552 11/15/05	13.5918	<2.4	<0.18	<0.16	11/28/2005
014A	SZ050553 11/15/05	13.8498	<2.4	<0.17	<0.16	11/28/2005
015A	SZ050554 11/15/05	13.0275	<2.4	<0.18	<0.17	11/28/2005

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: BK050502	Date Sampled: 11/2/2005
Lab Sample ID: S0511228-01A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 6:44:43 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 6:44:43 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 6:44:43 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 6:44:43 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 6:44:43 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 6:44:43 PM	JMM

Client Sample ID: BK050503	Date Sampled: 11/2/2005
Lab Sample ID: S0511228-02A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 6:47:44 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 6:47:44 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 6:47:44 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 6:47:44 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 6:47:44 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 6:47:44 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: SZ050504	Date Sampled: 11/2/2005
Lab Sample ID: S0511228-03A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref : NIOSH 7300 - METALS BY ICP
Air Vol(L): 162.87	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(ug/m³)	(ppm)				
Aluminum	<1.25	<0.00767	—	1.25	1	12/8/2005 6:56:50 PM	JMM
Barium	<0.250	<0.00153	—	0.250	1	12/8/2005 6:56:50 PM	JMM
Copper	2.21	0.0136	—	1.25	1	12/8/2005 6:56:50 PM	JMM
Lead	<0.625	<0.00384	—	0.625	1	12/8/2005 6:56:50 PM	JMM
Nickel	<0.625	<0.00384	—	0.625	1	12/8/2005 6:56:50 PM	JMM
Zinc	<1.25	<0.00767	—	1.25	1	12/8/2005 6:56:50 PM	JMM

Client Sample ID: SZ050505	Date Sampled: 11/2/2005
Lab Sample ID: S0511228-04A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref : NIOSH 7300 - METALS BY ICP
Air Vol(L): 165.438	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(ug/m³)	(ppm)				
Aluminum	<1.25	<0.00756	—	1.25	1	12/8/2005 6:59:54 PM	JMM
Barium	<0.250	<0.00151	—	0.250	1	12/8/2005 6:59:54 PM	JMM
Copper	4.43	0.0268	—	1.25	1	12/8/2005 6:59:54 PM	JMM
Lead	<0.625	<0.00378	—	0.625	1	12/8/2005 6:59:54 PM	JMM
Nickel	<0.625	<0.00378	—	0.625	1	12/8/2005 6:59:54 PM	JMM
Zinc	<1.25	<0.00756	—	1.25	1	12/8/2005 6:59:54 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: SZ050506	Date Sampled: 11/2/2005
Lab Sample ID: S0511228-05A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): 162.75	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Aluminum	<1.25	<0.00766	—	1.25	1	12/8/2005 7:02:57 PM	JMM
Barium	<0.250	<0.00154	—	0.250	1	12/8/2005 7:02:57 PM	JMM
Copper	3.30	0.0202	—	1.25	1	12/8/2005 7:02:57 PM	JMM
Lead	<0.625	<0.00384	—	0.625	1	12/8/2005 7:02:57 PM	JMM
Nickel	<0.625	<0.00384	—	0.625	1	12/8/2005 7:02:57 PM	JMM
Zinc	<1.25	<0.00766	—	1.25	1	12/8/2005 7:02:57 PM	JMM

Client Sample ID: BK050517	Date Sampled: 11/3/2005
Lab Sample ID: S0511228-06A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 7:05:59 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 7:05:59 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 7:05:59 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 7:05:59 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 7:05:59 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 7:05:59 PM	JMM

**Air Metals Report of Analysis
for
USAF CLINIC MCGUIRE/SGP**

WorkOrder: S0511228
Project:
Date Reported: 12/13/2005

Client Sample ID: BK050518	Date Sampled: 11/3/2005
Lab Sample ID: S0511228-07A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 7:09:02 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 7:09:02 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 7:09:02 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 7:09:02 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 7:09:02 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 7:09:02 PM	JMM

Client Sample ID: SZ050519	Date Sampled: 11/3/2005
Lab Sample ID: S0511228-08A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): 107.12	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 9:30

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Aluminum	<1.25	<0.0117	—	1.25	1	12/8/2005 7:12:05 PM	JMM
Barium	<0.250	<0.00233	—	0.250	1	12/8/2005 7:12:05 PM	JMM
Copper	<1.25	<0.0117	—	1.25	1	12/8/2005 7:12:05 PM	JMM
Lead	<0.625	<0.00583	—	0.625	1	12/8/2005 7:12:05 PM	JMM
Nickel	<0.625	<0.00583	—	0.625	1	12/8/2005 7:12:05 PM	JMM
Zinc	<1.25	<0.0117	—	1.25	1	12/8/2005 7:12:05 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: SZ050520	Date Sampled: 11/3/2005
Lab Sample ID: S0511228-09A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): 101.612	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	<0.0123	—	1.25	1	12/8/2005 7:24:24 PM	JMM
Barium	<0.250	<0.00246	—	0.250	1	12/8/2005 7:24:24 PM	JMM
Copper	<1.25	<0.0123	—	1.25	1	12/8/2005 7:24:24 PM	JMM
Lead	<0.625	<0.00615	—	0.625	1	12/8/2005 7:24:24 PM	JMM
Nickel	<0.625	<0.00615	—	0.625	1	12/8/2005 7:24:24 PM	JMM
Zinc	<1.25	<0.0123	—	1.25	1	12/8/2005 7:24:24 PM	JMM

Client Sample ID: SZ050521	Date Sampled: 11/3/2005
Lab Sample ID: S0511228-10A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): 75.516	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	<0.0166	—	1.25	1	12/8/2005 7:33:31 PM	JMM
Barium	<0.250	<0.00331	—	0.250	1	12/8/2005 7:33:31 PM	JMM
Copper	<1.25	<0.0166	—	1.25	1	12/8/2005 7:33:31 PM	JMM
Lead	<0.625	<0.00628	—	0.625	1	12/8/2005 7:33:31 PM	JMM
Nickel	<0.625	<0.00628	—	0.625	1	12/8/2005 7:33:31 PM	JMM
Zinc	<1.25	<0.0166	—	1.25	1	12/8/2005 7:33:31 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: BK050540	Date Sampled: 11/15/2005
Lab Sample ID: S0511228-11A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref : NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 7:36:30 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 7:36:30 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 7:36:30 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 7:36:30 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 7:36:30 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 7:36:30 PM	JMM

Client Sample ID: BK050541	Date Sampled: 11/15/2005
Lab Sample ID: S0511228-12A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref : NIOSH 7300 - METALS BY ICP
Air Vol(L): NA	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	—	—	1.25	1	12/8/2005 7:39:30 PM	JMM
Barium	<0.250	—	—	0.250	1	12/8/2005 7:39:30 PM	JMM
Copper	<1.25	—	—	1.25	1	12/8/2005 7:39:30 PM	JMM
Lead	<0.625	—	—	0.625	1	12/8/2005 7:39:30 PM	JMM
Nickel	<0.625	—	—	0.625	1	12/8/2005 7:39:30 PM	JMM
Zinc	<1.25	—	—	1.25	1	12/8/2005 7:39:30 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: SZ050542	Date Sampled: 11/15/2005
Lab Sample ID: S0511228-13A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): 89.91	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	<0.0139	—	1.25	1	12/8/2005 7:42:30 PM	JMM
Barium	<0.260	<0.00278	—	0.250	1	12/8/2005 7:42:30 PM	JMM
Copper	<1.25	<0.0139	—	1.25	1	12/8/2005 7:42:30 PM	JMM
Lead	<0.625	<0.00695	—	0.625	1	12/8/2005 7:42:30 PM	JMM
Nickel	<0.625	<0.00695	—	0.625	1	12/8/2005 7:42:30 PM	JMM
Zinc	<1.25	<0.0139	—	1.25	1	12/8/2005 7:42:30 PM	JMM

Client Sample ID: SZ050543	Date Sampled: 11/15/2005
Lab Sample ID: S0511228-14A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref: NIOSH 7300 - METALS BY ICP
Air Vol.(L): 89.052	
Site Identifier: 0121Z	Approver: Juanita.Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m³)	(ppm)				
Aluminum	<1.25	<0.0140	—	1.25	1	12/8/2005 7:45:32 PM	JMM
Barium	<0.260	<0.00281	—	0.250	1	12/8/2005 7:45:32 PM	JMM
Copper	<1.25	<0.0140	—	1.25	1	12/8/2005 7:45:32 PM	JMM
Lead	<0.625	<0.00702	—	0.625	1	12/8/2005 7:45:32 PM	JMM
Nickel	<0.625	<0.00702	—	0.625	1	12/8/2005 7:45:32 PM	JMM
Zinc	<1.25	<0.0140	—	1.25	1	12/8/2005 7:45:32 PM	JMM

**Air Metals Report of Analysis
for**

USAF CLINIC MCGUIRE/SGP

WorkOrder: S0511228

Project:

Date Reported: 12/13/2005

Client Sample ID: SZ050544	Date Sampled: 11/15/2005
Lab Sample ID: S0511228-15A	Date Received: 11/22/2005
Sample Type: MCE Filter	Method Ref : NIOSH 7300 - METALS BY ICP
Air Vol.(L): 96.975	
Site Identifier: 0121Z	Approver: Juanita Gilliland
Sample Location: BLDG 2225A	
Prep: NIOSH 7300 SAMPLE PREP	Prep Date: 11/30/2005 13:10

Analyte	Concentration			Limit of Detection (ug)	DF	Date Analyzed	Initials
	(ug)	(mg/m ³)	(ppm)				
Aluminum	<1.25	<0.0129	—	1.25	1	12/8/2005 7:48:33 PM	JMM
Barium	<0.250	<0.00258	—	0.250	1	12/8/2005 7:48:33 PM	JMM
Copper	<1.25	<0.0129	—	1.25	1	12/8/2005 7:48:33 PM	JMM
Lead	<0.625	<0.00644	—	0.625	1	12/8/2005 7:48:33 PM	JMM
Nickel	<0.625	<0.00644	—	0.625	1	12/8/2005 7:48:33 PM	JMM
Zinc	<1.25	<0.0129	—	1.25	1	12/8/2005 7:48:33 PM	JMM

General Notes:

<: Less than the indicated limit of detection (LOD).

—: Information not available or not applicable.

The calculated concentration (mg/m³) was obtained using the collection volume provided on the analysis request form.

Appendix D-3: Analytical Air Sampling Results and Findings from Ellsworth AFB

Air Sampling Results from Ellsworth

Individual Sampled	Analyte	Sample Number	Task Exposure (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
Tower Instructor	HCN	PZ051065	< 0.13	< 0.0255	11	< 0.2
	Copper	PZ051063	0.238	0.0466	1	4.7
	Zinc	PZ051063	0.0276	0.0054	10	0.1
	NO2	PZ051068	< 0.216	< 0.0423	5.6	< 0.8
	NO	PZ051069	< 0.216	< 0.0423	30	< 0.1
	HCl	PZ051067	< 0.37	< 0.0725	--	
	Ammonia	PZ051066	< 1.1	< 0.2154	17	< 1.3
Firing Line Instructor	Ammonia	PZ051072	< 1.1	< 0.2154	17	< 1.3
	Phosgene	PZ051070	0.037	0.0072	0.4	1.8
	HCN	PZ051071	< 0.13	< 0.0255	11	< 0.2
	Copper	PZ051064	0.245	0.0480	1	4.8
	Zinc	PZ051064	0.0281	0.0055	10	0.1
	NO2	PZ051075	< 0.211	< 0.0413	5.6	< 0.7
	NO	PZ051074	< 0.211	< 0.0413	30	< 0.1
	HCl	PZ051073	< 0.4	< 0.0783	--	

Notes:

--Temperature and pressure at time of sampling was near STP; therefore, concentrations not adjusted.

-- There was no analysis on Brown for phosgene because his air sampling pump failed.

Findings from Ellsworth

a. The major compositional difference between the lead and frangible ammunition is the replacement of the lead with alternative metals. These alternative metals are typically in powder form during manufacturing, and nylon is used to bind the metals together. Our study focused on the alternative metals and potential combustion by-products of nylon (or plastic in general) that may be irritating.

b. Air samples collected during this survey for the selected hazardous materials show concentrations to be well below the applicable OELs. However, range personnel indicated that they periodically experience eye and nasopharyngeal irritation that lasts 2-3 hours after firing is completed.

c. Smoke tests showed a potential for backflow of particles into the shooter's position behind the red line. During the firing of M-16 frangible ammunition on 23 Aug 05, a light haze formed behind the red line approximately 30 minutes after the commencement of firing.

d. During sampling, winds varied from 17 – 22 knots with the wind blowing from the south (directly into the range). Air enters the range through the baffled side containment walls and the overhead baffles with no exhaust outlet behind the target backstop. This condition causes the formation of eddies (swirling air) to propagate up-range toward the shooters.

Appendix D-4: Analytical Air Sampling Results and Findings from Whiteman AFB

Whiteman AFB Air Sampling Results

	Sample #	Contaminant	Concentration (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
Steve Allen	PZ051091	Aluminum	0.021	0.004	10	0.0
	PZ051091	Copper	0.848	0.164	1	16.4
	PZ051091	Zinc	0.104	0.020	10	0.2
	PZ051106	HCN	< 0.213	< 0.026	11	< 0.2
	PZ051113	NH3	< 1.776	< 0.215	17.5	< 1.2
	PZ051120	HCl	< 0.716	< 0.087		
	PZ051126	NO2	< 0.411	< 0.050	5.6	< 0.9
	PZ051131	NO	< 0.411	< 0.050	30	< 0.2
	PZ051134	Phosgene	< 0.081	< 0.004	0.4	< 1.0
Michael Mugler	PZ051092	Aluminum	0.027	0.005	10	0.1
	PZ051092	Copper	1.051	0.204	1	20.4
	PZ051092	Zinc	0.129	0.025	10	0.3
	PZ051107	HCN	< 0.143	< 0.028	11	< 0.2
	PZ051115	NH3	< 1.073	< 0.208	17.5	< 1.2
	PZ051121	HCl	< 0.428	< 0.083		
	PZ051127	NO2	< 0.213	< 0.041	5.6	< 0.7
	PZ051132	NO	< 0.213	< 0.041	30	< 0.1
	PZ051135	Phosgene	< 0.021	< 0.004	0.4	< 1.0
William Diebold	PZ051093	Aluminum	0.023	0.004	10	0.0
	PZ051093	Copper	0.990	0.192	1	19.2
	PZ051093	Zinc	0.125	0.024	10	0.2
	PZ051109	HCN	< 0.344	< 0.029	11	< 0.2
	PZ051116	NH3	< 2.438	< 0.208	17.5	< 1.2
	PZ051122	HCl	< 0.811	< 0.069		
	PZ051128	NO2	< 0.481	< 0.041	5.6	< 0.7
	PZ051133	NO	< 0.481	< 0.041	30	< 0.1
	PZ051136	Phosgene	< 0.021	< 0.004	0.4	< 1.0

Figure 1. Air Sampling Results on Day 1.

Whiteman AFB Air Sampling Results

	Sample #	Contaminant	Concentration (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
Mason Still	PZ051094	Aluminum	0.024	0.004	10	0.0
	PZ051094	Copper	0.035	0.006	1	0.6
	PZ051094	Zinc	0.016	0.003	10	0.0
	PZ051123	HCl	< 0.475	< 0.077		
	PZ051110	HCN	< 0.154	< 0.025	11	< 0.2
	PZ051129	NO2	< 0.063	< 0.010	5.6	< 0.2
	PZ051117	NH3	< 1.278	< 0.208	17.5	< 1.2
	PZ051137	Phosgene	< 0.026	< 0.004	0.4	< 1.1
William Diebold	PZ051095	Aluminum	0.029	0.005	10	0.0
	PZ051095	Copper	0.075	0.012	1	1.2
	PZ051095	Zinc	0.027	0.004	10	0.0
	PZ051124	HCl	< 0.434	< 0.070		
	PZ051111	HCN	< 0.153	< 0.025	11	< 0.2
	PZ051130	NO2	< 0.061	< 0.010	5.6	< 0.2
	PZ051118	NH3	< 1.278	< 0.208	17.5	< 1.2
	PZ051138	Phosgene	< 0.025	< 0.004	0.4	< 1.0
Area	PZ051096	Aluminum	0.043	0.005	10	0.0
	PZ051096	Copper	1.040	0.113	1	11.3
	PZ051096	Zinc	0.139	0.015	10	0.2
	PZ051125	HCl	< 0.769	< 0.083		
	PZ051112	HCN	< 0.260	< 0.028	11	< 0.2
	PZ051119	NH3	< 1.920	< 0.208	17.5	< 1.2
	PZ051139	Phosgene	< 0.038	< 0.004	0.4	< 1.0

Figure 2. Air Sampling Results on Day 2.

Findings from Whiteman

a. The major compositional difference between the lead and frangible ammunition is the replacement of the lead with alternative metals. These alternative metals are typically in powder form during manufacturing, and nylon is used to bind the metals together. Our study focused on the alternative metals and potential combustion by-products of nylon (or plastic in general) that may be irritating.

b. Air samples collected during this survey for the selected hazardous materials show concentrations to be well below the applicable OELs. However, range personnel indicated that students periodically experience eye and nasopharyngeal irritation after firing is completed.

c. A smoke generator was used to observe airflow pattern within the firing range prior to air sampling. Observations were made under three separate conditions: all doors open, all doors closed, and a combination of doors open and closed. Smoke tests showed a potential for backflow of particles into the shooter's position behind the red line if all doors were closed or doors open with at least 1 door closed. With all the doors open, the smoke propagated down range away from the shooter's position. Worst case conditions were observed with all doors closed as the smoke lingered in the shooter's breathing zone.

Appendix D-5: Analytical Air Sampling Results and Findings from Offutt AFB

Offutt Air Sampling Results

7-Nov	Sample #	Contaminant	Concentration (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
SSgt Serventi	1175	Aluminum	0.010	0.002	10	< 0.0
	1175	Copper	0.288	0.054	1	5.4
	1175	Zinc	0.032	0.006	10	0.1
	1187	HCN	< 0.073	< 0.014		
	1193	NH3	< 1.159	< 0.217	17.5	< 1.2
	1181	HCl	< 4.507	< 0.845		
	1206	NO2	< 0.225	< 0.042	5.6	< 0.8
	1200	NO	< 0.118	< 0.022	30	< 0.1
	1212	Phosgene	< 0.023	< 0.004	0.4	< 1.1
9-Nov	Sample #	Contaminant	Concentration (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
SSgt Serventi	1177	Aluminum	0.007	< 0.002	10	< 0.0
	1177	Copper	0.066	0.017	1	1.7
	1177	Zinc	0.008	0.002	10	0.0
	1183	HCl	< 0.230	< 0.058		
	1189	HCN	< 0.099	< 0.025		
	1202	NO	< 0.719	< 0.180	30	< 0.6
	1208	NO2	< 0.352	< 0.088	5.6	< 1.6
	1196	NH3	< 0.835	< 0.209	17.5	< 1.2
	1214	Phosgene	< 0.017	< 0.004	0.4	< 1.1
SSgt Eaton	1176	Aluminum	0.007	< 0.002	10	< 0.0
	1176	Copper	0.010	0.003	1	0.3
	1176	Zinc	0.007	< 0.002	10	< 0.0
	1182	HCl	< 0.225	< 0.056		
	1188	HCN	< 0.101	< 0.025		
	1201	NO	< 0.668	< 0.167	30	< 0.6
	1207	NO2	< 0.159	< 0.040	5.6	< 0.7
	1195	NH3	< 0.827	< 0.207	17.5	< 1.2
Area	1213	Phosgene	< 0.018	< 0.004	0.4	< 1.1
	1178	Aluminum	0.064	< 0.011	10	< 0.1
	1178	Copper	0.560	0.095	1	9.5
	1178	Zinc	0.065	0.011	10	0.1
	1184	HCl	< 0.315	< 0.064		
	1190	HCN	< 0.122	< 0.025		
	1203	NO	< 0.866	< 0.177	30	< 0.6
	1209	NO2	< 0.206	< 0.042	5.6	< 0.8
	1197	NH3	< 1.049	< 0.214	17.5	< 1.2
	1215	Phosgene	< 0.021	< 0.004	0.4	< 1.1

Figure 1. Air Sampling Results.

Atch 3 (1 of 3)

Offutt Air Sampling Results (Continued)

Cascade Impactors

Date	Sample #	Contaminant	Concentration (mg/m3)	8-Hour TWA Results (mg/m3)	TWA Standard (mg/m3)	% OEL
7-Nov	1143-1150	Copper	0.553	0.104	10	1
9-Nov	1151-1158	Copper	0.091	0.023	1	2.3
9-Nov	1159-1166	Copper	0.096	0.024	10	0.2

Air Quality Meters

Date	Contaminant	Minimum (ppm)	Maximum (ppm)	Average (ppm)
7-Nov	NO	0	1	0.2
7-Nov	NO2	0	0	0
7-Nov	CO	0	62	8
9-Nov	NO	0	0.8	0.2
9-Nov	NO2	0	0	0
9-Nov	CO	0	103	5

Figure 2. Air sampling results from the cascade impactor and the air quality meter. The air quality was measured with Quest aq-5000 monitors. The carbon monoxide 4CF CiTiceL sensors in the aq-5000 monitors were made by City Technology Ltd.

Findings from Whiteman

a. The major compositional difference between the lead and frangible ammunition is the replacement of the lead with alternative metals. These alternative metals are typically in powder form during manufacturing, and nylon is used to bind the metals together. Our study focused on the alternative metals and potential combustion by-products of nylon (or plastic in general) that may be irritating.

b. Air samples collected during this survey for the selected hazardous materials show concentrations to be well below the applicable OELs. However, range personnel indicated that instructors periodically (typically on calm days) experience eye and nasopharyngeal irritation after firing is completed. Additionally, some instructors experience a metallic taste in their mouth. This is more pronounced with instructors who smoke.

c. A smoke generator was used to observe airflow pattern within the firing range prior to air sampling. Observations were made with all doors closed and weather reported winds from 110 at 6 knots. The smoke generator was placed at position 8 and position 19. The smoke traveled toward position 1 and accumulated around shooting positions 3-6 and 1-10 respectively. Smoke tests showed a potential for backflow of particles into the shooter's position behind the red line.

d. Wind speed and direction (see attachment 2) directly influence the potential for exposure. Although there were more shooters and more rounds fired on 9 Nov, the measured copper concentration on 7 Nov was approximately 3 times greater than copper concentrations measured on 9 Nov. The wind on 7 Nov blew directly into the range, creating a positive pressure at the bullet trap. This caused the aerosols generated during firing to be pushed back towards the shooters/instructors. On 9 Nov, the wind blew across the range, pushing the aerosols towards the wall, minimizing exposure to shooters/instructors in the center of the range.

Appendix E: List of Equipment Used

Primary Flow Standards	Serial Number	Last Calibration	
BIOS Dry Cal DC-2	B1268	2 Oct 02	
BIOS Dry Cal Low Cell (DC-LC-1)	L1736	2 Oct 02	
BIOS Dry Cal Med Cell (DC-MC-1)	S3676	2 Oct 02	
 Air Sampling Pumps			
Gillian Hi Flow Sampler Model : HFS-513A	112.136		
Gillian Hi Flow Sampler Model : HFS-513A	112.139		
Gillian Hi Flow Sampler Model : HFS-513A	112.14		
 GILAIR-5 Tri-Mode Air Sampler	13184		
GILAIR-5 Tri-Mode Air Sampler	13193		
GILAIR-5 Tri-Mode Air Sampler	13520		
GILAIR-5 Tri-Mode Air Sampler	13873		
GILAIR-5 Tri-Mode Air Sampler	14679		
 SKC Pocket Pump 210-1002 (Hill AFB)	5872		
AirCheck Sampler (McGuire AFB)	545346		
 Indoor Air Quality Meter (Hill AFB)			
TSI Q-TRAK Model #8551	30497	Jul 04	
		21 Sep 05	(User Cal)
 Velometer (McGuire AFB)			
TSI ALNOR CompuFlow 8585	99017049	27 Apr 05	

Appendix F-1 NIOSH Method 7300 for Elements

ELEMENTS by ICP (Nitric/Perchloric Acid Ashing)

7300

MW: Table 1

CAS: Table 2

RTECS: Table 2

METHOD: 7300, Issue 3		EVALUATION: PARTIAL		Issue 1: 15 August 1990 Issue 3: 15 March 2003		
OSHA: Table 2 NIOSH: Table 2 ACGIH: Table 2		PROPERTIES: Table 1				
ELEMENTS:		aluminum* antimony* arsenic barium beryllium* cadmium	calcium chromium* cobalt* copper iron lead*	lanthanum lithium* magnesium manganese* molybdenum*	nickel potassium phosphorus selenium silver strontium tellurium tin thallium titanium	tungsten* vanadium* yttrium zinc zirconium*
*Some compounds of these elements require special sample treatment.						
SAMPLING			MEASUREMENT			
SAMPLER:	FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride membrane)		TECHNIQUE:	INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)		
FLOWRATE:	1 to 4 L/min		ANALYTE:	elements above		
VOL-MIN:	Table 1		ASHING			
-MAX:	Table 1		REAGENTS:	conc. HNO ₃ / conc. HClO ₄ (4:1), 5 mL; 2mL increments added as needed		
SHIPMENT:	routine		CONDITIONS:	room temperature, 30 min; 150 °C to near dryness		
SAMPLE STABILITY:	stable		FINAL SOLUTION:	4% HNO ₃ , 1% HClO ₄ , 25 mL		
BLANKS:	2 to 10 field blanks per set		WAVELENGTH:	depends upon element; Table 3		
ACCURACY			BACKGROUND CORRECTION:	spectral wavelength shift		
RANGE STUDIED:	not determined		CALIBRATION:	elements in 4% HNO ₃ , 1% HClO ₄		
BIAS:	not determined		RANGE:	varies with element [1]		
OVERALL PRECISION (S _{rel}):	not determined		ESTIMATED LOD:	Tables 3 and 4		
ACCURACY:	not determined		PRECISION (S):	Tables 3 and 4		
APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m ³ for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.						
INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].						
OTHER METHODS: This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.						

REAGENTS:

1. Nitric acid (HNO_3), conc., ultra pure.
2. Perchloric acid (HClO_4), conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO_3 : HClO_4 . Mix 4 volumes conc. HNO_3 with 1 volume conc. HClO_4 .
4. Calibration stock solutions, 1000 $\mu\text{g/mL}$. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3 , 1% HClO_4 . Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled, deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8- μm pore size; or polyvinyl chloride membrane, 5.0- μm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10-, 25-, 100-mL, and 1-L**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO₃/1% HClO₄:
 - a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
 - b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Ti, V, Y, Zn, Sc
 - c. Mo, Sb, Sn, Te, Ti, W, Zr
 - d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked blank filters per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m³), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{mg} / \text{m}^3$$

NOTE: µg/L = mg/m³

EVALUATION OF METHOD:**Issues 1 and 2**

Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

Issue 3

In this update of NIOSH Method 7300, the precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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METHOD REVISED BY:

Mark Millson and Ronnee Andrews, NIOSH/DART.

Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Laboratories, Salt Lake City, UT.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties		Air Volume, L @ OSHA PEL	
	Atomic Weight	MP, °C	MIN	MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.34	710	50	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Potassium (K)	39.10	63.65	5	1000
Lanthanum	138.91	920	5	1000
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Tungsten (W)	183.85	3410	5	1000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m ³ (Ca = carcinogen)		
			OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	—	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	—	—	—
Lanthanum	7439-91-0	—	—	—	—
Lithium (Li)	7439-93-2	—	—	—	—
Magnesium (Mg)	7439-95-4	OM2100000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	—	—	—	—
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	—	—	—
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW2400000	—	C 0.05	—
Tungsten	7440-33-7	—	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	—	—	—
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

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TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45 µm)

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
Sb	206	0.192	7.7	3.08	90.2	11.4	12.9	41.3	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
Sn	189	0.040	1.6	0.77	90.2	18.0	3.21	49	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
W	207	0.075	3.0	1.54	72.2	10.1	6.40	57.6	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
Zr	339	0.022	0.9	0.31	88.0	19.4	1.29	25	57.87

(a) Bold values are qualitative only because of low recovery.

(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD

(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified ¹⁷ 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
Ca	317	0.908	36.3	15.6	68.1	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
La	408	0.048	1.9	0.78	45.5	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
Mg	279	0.098	3.9	1.56	54.8	20.59	6.40	64.5	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
Sb	206	0.192	7.7	3.10	64.6	22.54	12.70	38.1	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
Sn	189	0.040	1.6	0.78	85.7	27.29	3.18	52.0	29.4
Sr	407	0.005	0.2	0.31	71.8	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
W	207	0.075	3.0	1.56	74.9	15.79	6.40	44.7	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
Zr	339	0.022	0.9	0.31	70.7	54.20	1.27	40.4	42.1

- (a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
- (b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
- (c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.

Appendix F-2 NIOSH Method S347 for Ammonia

Ammonia

Analyte:	Ammonia	Method No.: S347
Matrix:	Air	Range: 17-68 mg/cu m
OSHA Standard:	50 ppm (35 mg/cu m)	Precision (\overline{CV}_T): 0.062
Procedure:	Adsorption on sulfuric acid-treated silica gel, desorption with 0.1 N sulfuric acid, ammonia specific electrode	Validation Date: 11/25/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing sulfuric acid-treated silica gel to trap ammonia vapors. The sampling tube is connected in series to a prefilter to collect particulate ammonium salts.
- 1.2 Ammonia is desorbed from the silica gel with 0.1 N sulfuric acid, and the sample is analyzed using an ammonia specific electrode.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 16.9-67.6 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 759 mm Hg, using a 30-liter sample. This sample size is based on the capacity of the sulfuric acid-treated silica gel to collect vapors of ammonia in air at high relative humidity. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the sulfuric acid-treated silica gel. This capacity varies with the concentrations of ammonia and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 200 mg of sulfuric acid-treated silica gel) reaches 5% of the concentration in the test gas mixture. Breakthrough was not observed after 310 minutes at an average sampling rate of 0.209 liter/minute and relative humidity of 85% and temperature of 25°C. The breakthrough test was conducted at an average concentration of 68.6 mg/cu m.

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3. Interferences

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Methyl amine and ethyl amine are known interferences of the analytical method. Other volatile amines may also interfere in the analytical method.
- 3.3 Particulate contaminants such as ammonium salts are removed by the prefilter.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (\overline{CV}_T) for the total analytical and sampling method in the range of 16.9-67.6 mg/cu m is 0.062. This value corresponds to a 2.2 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.
- 4.2 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 2.4% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 33.8 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. The tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of micrograms that the tube will hold before overloading. When the amount of ammonia found on the backup section of the sulfuric acid-treated silica gel tube exceeds 25% of that found on the front section, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 Prefilter Unit: The prefilter unit, which is used to remove particulate interferences, consists of a 37-mm diameter cellulose ester membrane filter with a pore size of 0.80 micrometer contained in a 37-mm two-piece cassette filter holder. The filter is supported in the holder by a stainless steel screen.
- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.
- 6.3 Sulfuric Acid-Treated Silica Gel Sampling Tubes: Glass tube with both ends unsealed and fire-polished, 6.0-cm long with a 6-mm O.D. and a 4-mm I.D. containing two sections of 20/40 mesh sulfuric acid-treated silica gel (Section 8.2) separated by a 2-mm portion of glass wool. The adsorbing section of the tube contains 200 mg of sulfuric acid-treated silica gel and the backup section contains 100 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be no greater than 13 inches of water at a flow rate of 0.2 liter/minute. The glass tubes should be rinsed and dried with acetone before packing. The tubes are capped with plastic caps.
- 6.4 Orion Model 95-10 ammonia gas sensing electrode, or equivalent.
- 6.5 Orion Model 407 specific ion meter, or equivalent. A pH meter with a millivolt readout can also be used.
- 6.6 Scintillation vials, 20 mL.
- 6.7 Magnetic stirrer and stirring bars.
- 6.8 Pipets: Delivery type of convenient sizes.
- 6.9 Volumetric Flasks: 1-liter and 50-mL and other convenient sizes for preparing standard solutions.
- 6.10 Beakers, 250 mL.
- 6.11 Gas-tight syringes: 2- and 5-mL for preparing spiked samples.
- 6.12 Stopwatch.
- 6.13 Manometer.

7. Reagents

Whenever possible, reagents used must be ACS Reagent Grade or better.

- 7.1 Lecture bottle of ammonia gas, reagent grade.
- 7.2 Ammonium chloride, reagent grade.
- 7.3 Sulfuric acid, reagent grade in the following concentrations: 0.1 N and 0.4 N.

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- 7.4 Prepare a 1000 micrograms/mL ammonia stock standard by weighing 3.1476 g ammonium chloride in a 1-liter volumetric flask. Make to volume with deionized water.
- 7.5 Prepare a 10,000 micrograms/mL ammonia stock standard by weighing 31.476 g ammonium chloride in a 1-liter volumetric flask. Make to volume with deionized water.
- 7.6 Sodium hydroxide solution, 10 N.
- 7.7 Silica gel, 20/40 mesh from SKC, Inc.
8. Procedure
- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.
- 8.2 Preparation of Sulfuric Acid-Treated Silica Gel
- 8.2.1 Place 6 g of 20/40 mesh silica gel in a 250-mL beaker.
- 8.2.2 Add 15 mL of 0.4 N sulfuric acid to the beaker. Stir the mixture, and cover the beaker with a watch glass.
- 8.2.3 Heat the silica gel-acid mixture in a fume hood with a Bunsen burner to a very gentle boil. Evaporate approximately one-half of the liquid.
- 8.2.4 Place the covered beaker in a drying oven at 120°C until the remainder of the water has been evaporated.
- 8.2.5 The prepared acid-treated silica gel should flow freely and not adhere to the beaker. Store the silica gel in a desiccator until ready for use.
- 8.3 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative sampling tube and prefilter cassette unit in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.4 Collection and Shipping of Samples
- 8.4.1 Assemble the filter in the cassette holder and close firmly. The filter is backed up by a stainless steel screen rather than a filter pad. Secure the cassette holder with tape or shrinkable band.
- 8.4.2 Immediately before sampling, remove the caps from the ends of the sulfuric acid-treated silica gel tube. Remove the filter holder plugs and attach the outlet of the filter holder to the inlet of the sampling tube with a short piece of flexible tubing.

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- 8.4.3 The smaller section of sulfuric acid-treated silica gel is used as a backup and should be positioned nearer the sampling pump.
- 8.4.4 The tube should be placed in a vertical direction during sampling to minimize channeling through the sulfuric acid-treated silica gel.
- 8.4.5 Air being sampled should not pass through any hose or tubing before entering the prefilter cassette.
- 8.4.6 A sample size of 30 liters is recommended. Sample at a flow rate between 0.1 and 0.2 liter/minute. Record the sampling time, flow rate, and type of sampling pump used.
- 8.4.7 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.4.8 The sampling tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.4.9 The filter should be removed from the cassette filter holder and discarded. The cassette holders and stainless steel screens should be cleaned and saved for future use.
- 8.4.10 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank. A minimum of 18 extra sulfuric acid-treated silica gel tubes should be provided for desorption efficiency determinations.
- 8.4.11 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.5 Analysis of Samples

The meter used in the analysis of samples must be calibrated before samples are analyzed. The procedure for calibration of the specific ion meter or pH/millivolt meter is discussed in Section 9. Proceed to Section 9 before sample analysis.

- 8.5.1 Preparation of Samples. Remove the plastic cap from the inlet end of the sampling tube. Remove the glass wool plug and transfer the first (larger) section of sulfuric acid-treated silica gel to a 20-mL scintillation vial. Remove the separating section of glass wool and transfer the backup section of sulfuric acid-treated silica gel to another scintillation vial. Analyze these two sections separately. Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.

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- 8.5.2 Desorption of Samples. Prior to analysis, 10 mL of 0.1 N sulfuric acid is pipetted into each vial. Cap and shake the sample vigorously. Desorption is complete in 45 minutes. Analyses should be completed within one day after the ammonia is desorbed.
- 8.5.3 Pipet an 8-mL aliquot of the desorbed sample into a clean 20-mL scintillation vial. Add 6 mL of deionized water to the vial.
- 8.5.4 Add 1 mL of 10 N sodium hydroxide to the vial to make the solution basic. The total volume in the vial should be 15 mL. Add a magnetic stirring bar. After addition of base, samples should be analyzed immediately.
- 8.5.5 Lower the ammonia specific electrode into the solution, taking care not to trap air under the electrode. If using a specific ion meter, record the meter reading on the logarithmic scale. This reading is the sample concentration in micrograms/mL. If a pH/millivolt meter is used, record the millivolt reading and refer to the calibration curve prepared in Section 9 to determine the sample concentration.
- 8.5.6 If the sample falls outside of the range of analysis, recalibrate the meter in the range of interest.
- 8.6 Determination of Desorption Efficiency
- 8.6.1 The desorption efficiency of a particular compound can vary from one laboratory to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process.
- 8.6.2 Extra sampling tubes containing sulfuric acid-treated silica gel are used to prepare spiked samples for desorption efficiency determinations. Spiked samples are prepared by drawing air through the tubes and spiking the air upstream of the tube with the appropriate amount of ammonia gas. Ammonia gas is spiked upstream using gas tight syringes. Volumes of 0.755, 1.51, and 3.02 mL of ammonia gas represent the amount present at 0.5X, 1X, and 2X the OSHA standard levels, respectively. The amount spiked is equivalent to that present in a 30-liter air sample at the selected level.
- Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to ensure complete adsorption of the ammonia onto the sulfuric acid-treated silica gel. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.5.

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The desorption efficiency (D.E.) equals the average weight in micrograms recovered from the tube divided by the weight in micrograms added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (micrograms)} - \text{Blank}}{\text{Weight added (micrograms)}}$$

The desorption efficiency is dependent on the amount of ammonia collected on the sulfuric acid-treated silica gel. Plot the desorption efficiency versus weight of ammonia found. This curve is used in Section 10.5 to correct for adsorption losses.

9. Calibration and Standards

- 9.1 Prepare standard solutions containing 10 micrograms/mL, 100 micrograms/mL, and 1000 micrograms/mL as described below:

- 9.1.1 10 micrograms/mL: Using the 1000 micrograms/mL stock solution (Section 7.4), pipet a 5-mL aliquot into a 50-mL volumetric flask and bring to volume with deionized water. From this solution, pipet another 5-mL aliquot into a clean 50-mL volumetric flask, and add 20 mL 0.1 N sulfuric acid, 2 mL of 10 N sodium hydroxide, and bring to volume with deionized water. This final solution is the 10 micrograms/mL standard. Cap the solution after preparation.
- 9.1.2 100 micrograms/mL: Pipet a 5-mL aliquot from the 1000 micrograms/mL stock solution into a clean 50-mL volumetric flask. Add 20 mL 0.1 N sulfuric acid, 2 mL 10 N sodium hydroxide, and bring to volume with deionized water. Cap the solution after preparation.
- 9.1.3 1000 micrograms/mL: Pipet a 5-mL aliquot from the 10,000 micrograms/mL stock solution (Section 7.5) into a clean 50-mL volumetric flask. Add 20 mL 0.1 N sulfuric acid, 2 mL 10 N sodium hydroxide, and bring to volume with deionized water. Cap the solution after preparation.

Note: These standards are good for approximately 2 hours if kept tightly capped.

Additional standards may be prepared in order to accommodate the range of samples to be analyzed. Prepare additional standards over the range of interest using the 1000 micrograms/mL stock standard solution.

- 9.2 The specific ion meter must be calibrated over the range of interest using standard solutions prepared as described above. The meter is calibrated over a 10-fold concentration range.

To calibrate the specific ion meter in the range of 10-100 micrograms/mL, use the following procedure:

- 9.2.1 Place the electrode in the 10 micrograms/mL standard. Turn the function switch to X⁻ and adjust the meter needle to "10" on the logarithmic scale with the calibration control. Use magnetic stirring throughout the procedure.
 - 9.2.2 Rinse the electrode and place in the 100 micrograms/mL standard and stir thoroughly. Turn the temperature compensator knob until the meter needle reads "100" on the logarithmic scale. The meter is now calibrated in the range of 10-100 micrograms/mL.
 - 9.2.3 Recalibration of the meter is necessary in order to analyze samples outside of this range. Repeat the calibration procedure for the range of 100-1000 micrograms/mL.
- 9.3 If a pH/millivolt meter is used, the standards described above can be used to prepare a standard calibration curve. The curve is prepared on semi-log paper by plotting millivolt versus concentration in micrograms/mL. The concentration should be plotted on the logarithmic scale.

10. Calculations

- 10.1 Read the concentration, in micrograms/mL, corresponding to each meter reading.

- 10.2 Corrections for the blank must be made for each sample.

$$\text{micrograms/mL} = \text{micrograms/mL sample} - \text{micrograms/mL blank}$$

where:

$$\text{micrograms/mL sample} = \text{micrograms/mL found in front section of sample tube}$$

$$\text{micrograms/mL blank} = \text{micrograms/mL found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

- 10.3 Determine the micrograms/sample by making the following volume correction.

$$\text{Micrograms/sample} = \text{micrograms/mL} \times 15 \text{ mL} \times \frac{10 \text{ mL}}{8 \text{ mL}}$$

- 10.4 Add the weights found in the front and backup sections to determine the total weight of the sample.

- 10.5 Read the desorption efficiency from the curve (see Section 8.6.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

- 10.6 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

- f = flow rate sampled
- t = sampling time
- P₁ = pressure during calibration of sampling pump (mm Hg)
- P₂ = pressure of air sampled (mm Hg)
- T₁ = temperature during calibration of sampling pump (°K)
- T₂ = temperature of air sampled (°K)

- 10.7 The concentration of ammonia in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected micrograms (Section 10.5)}}{\text{Corrected air volume (liters) (Section 10.6)}}$$

- 10.8 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

- P = pressure (mm Hg) of air sampled
- T = temperature (°C) of air sampled
- 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
- M.W. = molecular weight of ammonia
- 760 = standard temperature (°K)
- 298 = standard temperature (°K)

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- 11.2 Backup Data Report for Ammonia, prepared under NIOSH Contract No. 210-76-0123.

S347-9

Appendix F-3 NIOSH Method 6010 for Hydrogen Cyanide

HYDROGEN CYANIDE

6010

HCN MW: 27.03 CAS: 74-90-8 RTECS: MW6825000

METHOD: 6010, Issue 2		EVALUATION: FULL		Issue 1: 15 May 1989 Issue 2: 15 August 1994	
OSHA : 10 ppm (skin) NIOSH: STEL 4.7 ppm ACGIH: C 10 ppm (skin) (1 ppm = 1.105 mg/m ³ @ NTP)			PROPERTIES: gas; BP 26 °C; vapor density 0.93 (air = 1.00); d(liq) 0.69 g/mL @ 20 °C; VP 82.7 kPa (620 mm Hg) @ 20 °C; explosive range 5 to 40% v/v in air		
SYNONYMS: hydrocyanic acid, prussic acid, formonitrile					
SAMPLING			MEASUREMENT		
SAMPLER: SOLID SORBENT TUBE (soda lime, 600 mg/200 mg) FLOW RATE: 0.05 to 0.2 L/min VOL-MIN: 2 L @ 5 ppm -MAX: 90 L SHIPMENT: routine SAMPLE STABILITY: at least 2 weeks @ 25 °C [1] BLANKS: 2 to 10 field blanks per set			TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION ANALYTE: cyanide ion complex DESORPTION: 10 mL deionized water; stand 60 min COLOR DEVELOPMENT: N-chlorosuccinimide/ succinimide oxidizing agent and barbituric acid/pyridine coupling agent; absorption @ 580 nm in 1-cm cuvette CALIBRATION: standard solutions of KCN in 0.1 N NaOH RANGE: 10 to 300 µg CN ⁻ per sample [1] ESTIMATED LOD: 1 µg CN ⁻ per sample [1] PRECISION (S _p): 0.041 @ 10 to 50 mg per sample [1]		
ACCURACY					
RANGE STUDIED: 2 to 15 mg/m ³ [1] (3-L samples) BIAS: Not significant OVERALL PRECISION (S _{PT}): 0.076 [1] ACCURACY: ± 15.0%					
APPLICABILITY: The working range is 0.3 to 235 ppm (3 to 260 mg/m ³) for a 3-L air sample. This method is applicable to STEL measurements. Particulate cyanides are trapped by the initial glass fiber membrane disk. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904, which uses ion specific electrode analysis. The method was used to determine HCN in firefighting environments [2].					
INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference.					
OTHER METHODS: This is based on the method of Lambert, et al. [3]. NIOSH Method 7904 uses an ion specific electrode for measurement. The method has been adapted for use with a Technicon Autoanalyzer [4].					

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REAGENTS:

1. Potassium cyanide*, reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectrophotometric quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, concentrated, reagent grade.
8. Sodium hydroxide (NaOH), reagent grade.*
9. Sodium lime (CaO + 5-20% NaOH), reagent grade (Aldrich #26,643-4 or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
10. Water deionized-distilled.
11. Sodium hydroxide solution, 0.1 N.*
12. Calibration stock solution. 1 mg /mL CN⁻. Dissolve 0.125 g KCN in 0.1 N NaOH in a 50-mL volumetric flask. Dilute to mark with 0.1 N NaOH. Standardize by titration with standard AgNO₃ solution (see APPENDIX).
13. Hydrochloric acid solution, 0.15 N.
14. N-Chlorosuccinimide/succinimide oxidizing reagent. Dissolve 10.0 g succinimide in about 200 mL distilled water. Add 1.00 g N-chlorosuccinimide. Stir to dissolve. Adjust volume to 1 liter with distilled water. Stable 6 months when refrigerated.
15. Barbituric acid/Pyridine reagent. Add about 30 mL distilled water to 6.0 g barbituric acid in a 100-mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust the volume to 100 mL with water. Stable 2 months when refrigerated.

EQUIPMENT:

1. Sampler, glass tube, 9 cm long, 7-mm OD, 5-mm ID, with plastic caps, containing two sections (front = 600 mg; back = 200 mg) granular soda lime 10/35 mesh, separated and contained with silanized glass wool plugs, with a 5-mm diameter glass fiber filter disk placed before the plug on inlet side. Tubes are commercially available. (SKC, Inc. 226-28 or equivalent.)
2. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm light path.
3. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
4. Pipets, volumetric 0.1-, 0.5-, 1.0-, 2.0-, 10.0-mL.
5. Vials, glass or plastic, 15-mL with PTFE-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Syringes, 10-μL, readable to 0.1 μL.
9. Flask, Erlenmeyer, 100-mL.
10. Syringes, 10-mL, polyethylene with luer tip.
11. Filter cassette, with membrane filter, 13-mm diameter, 0.45-μm pore size, with luer fitting.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [5]. Soda lime and NaOH are very caustic [5]. Use gloves and a fume hood for handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
 2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
 4. Cap tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
 6. Transfer front and back sorbent sections to separate vials. Discard glass wool plugs separating and retaining sorbent sections.
- NOTE: An estimate of particulate cyanide may be obtained by analyzing the initial glass fiber filter disk as follows; however, no evaluation data are available for particulate cyanides determined in this manner.
- (i) Transfer the glass wool plug at the tube inlet and the glass fiber filter disk immediately behind it to a third vial.
 - (ii) Add 10.0 mL 0.1 N NaOH to each vial.
 - (iii) Proceed with step 8.
7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section. Cap each vial.
 8. Allow to stand 60 minutes, with occasional agitation. Transfer to a 10-mL plastic syringe fitted with an in-line 0.45- μ m filter. Collect the filtrate in a clean vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 1 to 300 μ g CN⁻ per sample.
 - a. Prepare a working standard solution, 1.00 μ g /mL CN⁻, by diluting 100 μ L of calibration stock solution to 100 mL with 0.1 N NaOH.
 - b. Pipet 0.5-, 1.00-, 1.50-, 2.00- and 2.50-mL of the working standard solution into 25-mL volumetric flasks to make 0.50-, 1.00-, 1.50-, 2.00- and 2.50- μ g CN⁻ standards.
 - c. Analyze together with field samples and blanks (steps 12 through 19).
 - d. Prepare calibration graph (absorbance vs. μ g CN⁻).
10. Determine desorption efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a blank sampler.
 - b. Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
 - c. Cap, and allow to stand overnight.
 - d. Desorb (steps 5 through 8) and analyze together with working standards and blanks (steps 12 through 19).
 - e. Prepare a graph of DE vs. μ g CN⁻ recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set spectrophotometer according to manufacturer's recommendations and to conditions on p. 6010-1.
13. Pipet a sample aliquot estimated to contain 0.5 to 2.5 μ g CN⁻ into a 25-mL volumetric flask. Alternately, to cover an unknown sample concentration range, pipet 0.5-, 1.00-, and 3.00-mL aliquots into separate 25-mL vol. flasks for each field sample. Larger or smaller aliquots may be taken, based on prior knowledge of expected analyte level.
14. Pipet 0.5 mL 0.1 N NaOH into a 25-mL volumetric flask for reagent blank.
15. Add one drop phenolphthalein solution to each standard or sample.
NOTE: Add a little deionized-distilled water to increase volume for easier mixing. All solutions should be alkaline (pink) at this point.
16. Starting with the reagent blank, add dropwise 0.15 N HCl, with mixing, until pink color just disappears. CAUTION: HCN may be produced. Work in hood. Immediately add 1.0 mL N-chlorosuccinimide/succinimide oxidizing reagent. Mix and let stand.

NOTE 1: To avoid possible loss of HCN, add the oxidizing agent before proceeding to the next sample.

NOTE 2: Do not prepare more samples than can be analyzed within the 30-minute maximum time for color development.

17. After at least 5 min. standing (but not longer than 15 min), starting with the reagent blank, add 1.0-mL barbituric acid-pyridine coupling reagent. Mix.
18. Adjust sample volume to 25 mL with deionized-distilled water and allow to stand at least 12 min (but not longer than 30 min) for color development.
19. Read absorbance at 580 nm in a 1-cm light path cuvette on a spectrophotometer. If sample absorbance is outside the range of the calibration standards, take an aliquot, re-analyze (steps 12 through 19), and apply the appropriate aliquot factor in calculations.

CALCULATIONS:

20. Calculate the mass, μg , of CN^- in aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, μg , of CN^- in the original 10-mL solution.
21. Determine the mass, μg CN^- (corrected for DE), found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections. If $W_b > W_f/10$, report breakthrough and possible sample loss.
22. Calculate concentration, C, of HCN in the air volume sampled, V(L).

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.039}{V}, \text{ mg/m}^3.$$

where 1.039 = conversion factor, CN^- to HCN

EVALUATION OF METHOD:

The method was evaluated by sampling the test atmospheres of HCN generated from a compressed mixture of HCN in nitrogen [1]. The range of HCN concentration was equivalent to 2 to 15 mg/m^3 for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision \bar{S}_r of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at the flow rate of 0.2 L/min at an HCN concentration of 148 mg/m^3 . Sample tubes spiked with solutions of KCN and analyzed after storage, indicated that the samples of cyanide ions were stable on the tube for at least 2 weeks. Analysis of 22 tubes which were spiked with KCN standard solutions in the range 10 to 50 μg indicated a recovery of nearly 100% with a pooled precision of 0.041. Desorption efficiency may be poor below 10 μg CN^- [6].

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METHOD WRITTEN BY: George Williamson, NIOSH/DPSE.

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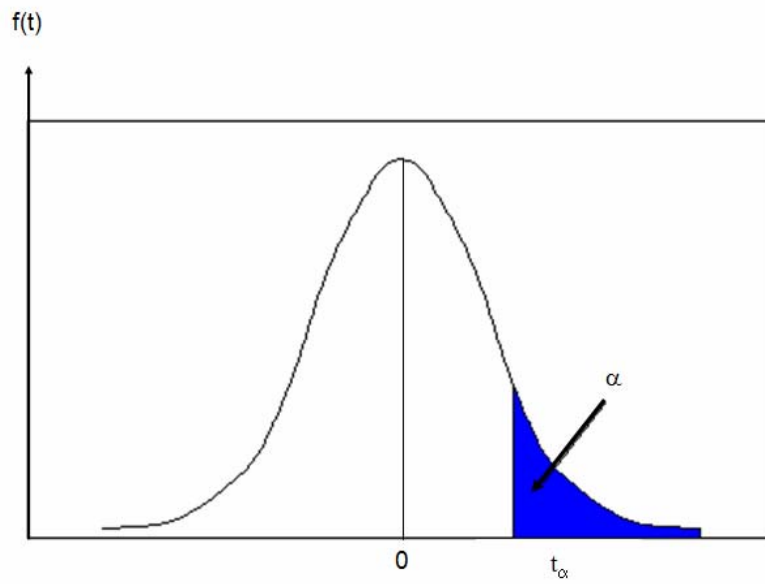
APPENDIX: STANDARDIZATION OF CALIBRATION STOCK SOLUTION

Titrate an aliquot of the cyanide standard stock solution (Reagent 12) with standard silver nitrate (AgNO_3) solution. The end point is the first formation of a white precipitate, $\text{Ag}[\text{Ag}(\text{CN})_2]$. Calculate the cyanide concentration with the following equation:

$$M_c = 52.04 V_s (M_s/V_c)$$

Where M_c = cyanide concentration (mg/mL)
 V_s = volume (mL) of standard silver nitrate solution
 M_s = concentration (moles/L) of standard silver nitrate solution
 V_c = volume (mL) of calibration stock solution titrated

Appendix G: Summary Table of Critical t-Values



Degrees of Freedom	$t_{.025}$	Degrees of Freedom	$t_{.025}$
1	12.706	18	2.101
2	4.303	19	2.093
3	3.182	20	2.086
4	2.776	21	2.080
5	2.571	22	2.074
6	2.447	23	2.069
7	2.365	24	2.064
8	2.306	25	2.060
9	2.262	26	2.056
10	2.228	27	2.052
11	2.201	28	2.048
12	2.179	29	2.045
13	2.160	30	2.042
14	2.145	40	2.021
15	2.131	60	2.000
16	2.120	120	1.980
17	2.110	Infinity	1.960

Appendix H-1: Summary of Results for Base Specific Outdoor Ranges

Table 4.9 Summary of Air Sampling Results for Ellsworth AFB

Analyte	Number of Samples	Task Exposure (mg/m ³)		Standard Deviation	8-Hr TWA (mg/m ³)		Standard Deviation
		Median	Mean		Median	Mean	
Ammonia	2	1.100	1.100	0.00E+00	0.215	0.215	0.00E+00
Copper	2	0.242	0.242	4.95E-03	0.047	0.047	9.90E-04
HCL	2	0.385	0.385	2.12E-02	0.075	0.075	4.10E-03
HCN	2	0.130	0.130	0.00E+00	0.026	0.026	0.00E+00
NO	2	0.214	0.214	3.54E-03	0.042	0.042	7.07E-04
NO2	2	0.214	0.214	3.54E-03	0.042	0.042	7.07E-04
Phosgene	1	0.037	0.037	0.00E+00	0.007	0.007	0.00E+00
Zinc	2	0.028	0.028	3.54E-04	0.005	0.005	7.07E-05

Table 4.10 Summary of Air Sampling Results for Whiteman AFB

Analyte	Number of Samples	Task Exposure (mg/m ³)		Standard Deviation	8-Hr TWA (mg/m ³)		Standard Deviation
		Median	Mean		Median	Mean	
Aluminum	6	0.026	0.028	7.96E-03	0.005	0.005	5.48E-04
Copper	6	0.919	0.673	4.84E-01	0.106	0.104	9.24E-02
HCL	6	0.596	0.606	1.78E-01	0.080	0.099	5.39E-02
HCN	6	0.184	0.211	7.92E-02	0.027	0.027	1.72E-03
NH3	6	1.527	1.627	5.13E-01	0.208	0.209	2.86E-03
NO	3	0.411	0.368	8.52E-02	0.041	0.044	5.20E-03
NO2	5	0.213	0.246	1.94E-01	0.041	0.039	3.06E-02
Phosgene	6	0.026	0.035	2.32E-02	0.004	0.004	0.00E+00
Zinc	6	0.115	0.090	5.44E-02	0.018	0.015	9.70E-03

Table 4.11 Summary of Air Sampling Results for McGuire AFB

Analyte	Number of Samples	Task Exposure (mg/m ³)		Standard Deviation	8-Hr TWA (mg/m ³)		Standard Deviation
		Median	Mean		Median	Mean	
Barium	9	0.00246	0.00232	6.53E-04	0.00040	0.00041	3.55E-05
Copper	9	0.01390	0.01578	4.88E-03	0.00235	0.00316	1.81E-03
Lead	9	0.00615	0.00579	1.63E-03	0.00097	0.00103	8.82E-05
Aluminum	9	0.01230	0.01159	3.27E-03	0.00200	0.00207	1.74E-04
Zinc	9	0.01230	0.01159	3.27E-03	0.00200	0.00207	1.74E-04
NH3	5	0.99500	1.09000	1.28E-01	0.16350	0.16529	4.15E-03
HCN	9	0.17000	0.16778	5.09E-02	0.02888	0.05367	2.55E-02

Table 4.12 Summary of Air Sampling Results for Offutt AFB

Analyte	Number of Samples	Task Exposure (mg/m ³)		Standard Deviation	8-Hr TWA (mg/m ³)		Standard Deviation
		Median	Mean		Median	Mean	
Aluminum	3	0.007	0.008	1.72E-02	0.002	0.002	2.76E-03
Copper	3	0.066	0.121	1.99E-01	0.017	0.025	3.40E-02
HCL	3	0.23	1.654	2.50E+00	0.058	0.320	4.62E-01
HCN	3	0.099	0.091	1.83E-02	0.025	0.021	6.45E-03
NH3	3	0.835	0.940	1.92E-01	0.209	0.211	5.37E-03
NO	3	0.719	0.751	2.19E-01	0.177	0.175	4.72E-02
NO2	3	0.225	0.245	9.88E-02	0.042	0.057	2.75E-02
Phosgene	3	0.018	0.019	3.25E-03	0.004	0.004	0.00E+00
Zinc	3	0.008	0.016	2.07E-02	0.002	0.003	3.29E-03

Appendix H-2: Summary of Results for Base Specific Indoor Ranges

Table 4.13 Summary of Air Sampling Results for Hill AFB

Analyte	Number of Samples	Median Task Exposure (mg/m ³)	Standard Deviation	95% CL (Task)		Mean 8-Hr TWA (mg/m ³)	Standard Deviation	95% CL (8-hour))	
				LCL	UCL			LCL	UCL
Barium	9	0.004	1.996	0.003	0.007	0.001	2.157	0.001	0.002
Copper	9	0.008	1.323	0.007	0.010	0.002	1.385	0.002	0.003
Lead	9	0.006	1.279	0.005	0.007	0.001	1.374	0.001	0.002
Tin	6	0.007	1.133	0.006	0.008	0.002	1.122	0.002	0.002
Zinc	9	0.009	1.703	0.006	0.014	0.002	1.801	0.001	0.004
NH3	9	0.850	1.283	0.702	1.030	0.212	1.253	0.179	0.253
HCN	9	0.152	1.130	0.139	0.167	0.038	1.044	0.037	0.039

Table 4.14 Summary of Air Sampling Results for Wright Patterson AFB

Analyte	Number of Samples	Median 8-Hr TWA (mg/m ³)	Standard Deviation	95% CL (8-hour))	
				LCL	UCL
Barium	4	0.001	1.483	0.000	0.001
Copper	9	0.012	2.198	0.006	0.021
Lead	9	0.001	1.276	0.001	0.001
Tin	4	0.002	1.845	0.001	0.006

Appendix H-3: Summary of Task Lead Exposure at Indoor Ranges Firing Leaded Ammunition

Table 4.15 Summary of Task Lead Exposures at Indoor Ranges Firing Leaded Ammunition

Sample Population	Analyte	Number of Samples	Median Task Exposure (mg/m ³)	Standard Deviation	95% CL (Task)		OEL (mg/m ³)	X OEL (Based on UCL)
					LCL	UCL		
M16 Only	Lead	28	0.0478	6.738	0.0228	0.1001	0.05	2
M16 Only *	Lead	26	0.0331	4.042	0.0188	0.0582	0.05	1.2
M16 & Unknown	Lead	78	0.0139	7.116	0.0089	0.0216	0.05	0.4
M16 & Unknown *	Lead	76	0.0118	5.585	0.0080	0.0175	0.05	0.4

* Excluding Samples 2 & 8 (Luke AFB)

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Vita

Captain Eric J. Cameron graduated from Oakmont High School in Roseville, California. He entered undergraduate studies at the University of California, Sacramento where he graduated with a Bachelor of Science degree in Civil Engineering in December 1997. In May 1998, he was commissioned into the United States Air Force through the Detachment 88 AFROTC at the University of California, Sacramento and was assigned to the 319th Aerospace Medicine Squadron, Grand Forks AFB, North Dakota as a Bioenvironmental Engineer. During his first assignment he competed and was selected to serve as an ambassador for the Air Force in the Air Force's Premiere Entertainment group, Tops in Blue. During this one year worldwide tour of duty, Captain Cameron entertained 280,000 soldiers and families and supervised a technical staff responsible for the unloading, setup, operation, teardown and reloading of 36,000 pounds of audio, lighting, and staging equipment for over 125 performances.

In March 2001, he was assigned to the 75th Aerospace Medicine Squadron, Hill AFB, Utah where he supervised 15 Bioenvironmental Engineering technicians as the Chief of the Industrial Hygiene Division for two F-16 fighter wings, one base wing, and the largest Air Force test and training range in the Continental United States. While stationed at Hill AFB, he deployed overseas to Prince Sultan Air Base, Saudi Arabia from September to December of 2002 as the Bioenvironmental Engineering Flight Commander. In August 2004, he entered the Graduate School of Systems and Engineering Management, Air Force Institute of Technology. Upon graduation, he will be assigned as an Air Force consultant for the Water and Wastewater Division at Brooks City Base, Texas.

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14. ABSTRACT This study examines airborne chemical exposure to Air Force small arms range instructors during M16 firing of lead and lead-free bullets. Historical range information collected from 63 active duty Air Force bases identified that two thirds of the Air Force military ranges within the Continental United States are currently firing lead-free ammunition. Average 8-hr TWA exposures for lead during M16 firing of leaded ammunition were 17% of the Occupational Exposure Limit (OEL). Task exposures, representing worst case conditions, were found to be 1.2 time the OEL. Two indoor and four outdoor firing ranges currently firing frangible lead-free ammunition were evaluated through a collaborative effort with the Air Force Institute for Operational Health (AFIOH) to assess instructor exposure and current range conditions. Transition to lead-free ammunition showed a 70% reduction in lead at indoor ranges and a 41% reduction in lead at outdoor ranges. Airborne exposures generated from metals and combustion by-products associated with nylon and plastics during M16 firing of frangible lead-free ammunition were found to be well below their respective OELs. This research suggests that the average exposure levels associated with lead-free ammunition does not pose a significant threat to Air Force instructors at indoor and outdoor ranges.					
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